



AEC Computing and Applied Mathematics Center

AEC RESEARCH AND DEVELOPMENT REPORT

TID-4500
5th Ed.

NYO-1480-20
PHYSICS

ASYMPTOTIC WAVE FUNCTIONS
FOR ATOMIC SYSTEMS

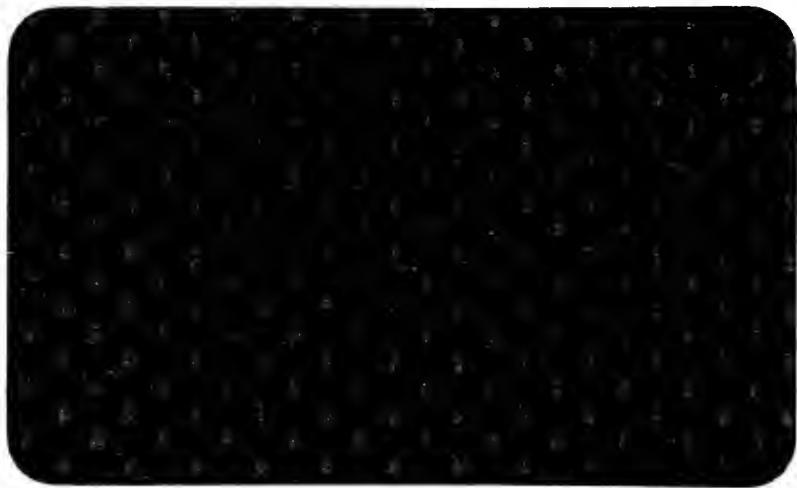
by

Lawrence Mendlsohn and Jerome Feinman

April 30, 1964

Courant Institute of Mathematical Sciences

NEW YORK UNIVERSITY
NEW YORK, NEW YORK



This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

UNCLASSIFIED

AEC Computing and Applied Mathematics Center
Courant Institute of Mathematical Sciences
New York University

TID-4500
39th Ed.

NYO-1480-20
PHYSICS

ASYMPTOTIC WAVE FUNCTIONS
FOR ATOMIC SYSTEMS
by

Lawrence Mendelsohn and Jerome Percus

April 30, 1965

TABLE OF CONTENTS

	Page
Abstract	3
Section	
1. Introduction	4
2. Asymptotic Solutions for Separable Atomic Systems	8
3. Asymptotic Solutions for General Atomic Systems .	13
4. Asymptotic Ground State Solutions for 2 Electron Atoms.	18
5. Expectation Values for 2 Electron Atomic Systems.	24
6. Technique of "Matched Asymptotic Expansions" . .	28
7. Solutions in the Neighborhood of Singular Points	33
Appendix	55
Figure 1	56
Figure 2	57
Figure 3	58
Figure 4	59
Figure 5	60
Bibliography	61

ABSTRACT

A new technique for calculating wave functions for atoms and ions is developed. Formal asymptotic expansions with largeness parameter Z (nuclear charge) are determined through first order in $1/Z$. In so doing the Schrodinger Equation for a general atomic system with N electrons is reduced to a set of first order partial differential equations which are solved recursively. Screening and correlation are exhibited explicitly in the resulting asymptotic atomic wave functions. Applications made to the ground state of 2 electron systems show that the asymptotic wave function obeys the virial theorem through first order. Magnetic susceptibilities within 5% of the accepted values are obtained for helium and singly ionized lithium. Other expectation values, $1/2(s_1 + s_2)$, s_{12}^2 and s_{12} are found to be in excellent agreement with a variational calculation utilizing 1078 parameters. In determining the asymptotic wave function in regions about certain singular points by a "matching technique", $\ln Z/Z$ terms enter. The omission of such terms in ordinary variational-perturbation wave functions may result in a loss of accuracy when computing expectation values other than the energy.

ASYMPTOTIC WAVE FUNCTIONS FOR ATOMIC SYSTEMS

1. Introduction.

Recently approximate ground state solutions to the nonrelativistic Schrodinger equation for many electron atoms have received considerable attention. Electron wave functions giving a reasonably correct description of the electron density throughout configuration space would facilitate calculation of weak interaction effects. Of late, there have been refinements in the experimental measurements of magnetic susceptibility, electric polarizability and quadrupole coupling of atoms. The utilization of more accurate wave functions would allow calculation of these effects to keep pace with experiment. More accurate atomic scattering factors could also be obtained. In addition, if accurate excited state wave functions were known, transition probabilities and optical absorption and inelastic scattering cross-sections could be calculated with much greater precision.

The calculation of ground state atomic wave functions is usually performed by either a Hartree (Hartree-Fock) calculation or by some other variational technique. It is well known that Hartree calculations usually give the energy of the ground state to within 1 per cent.¹ However these solutions do not incorporate interelectronic repulsion correctly since they describe each electron as moving in the average central field due to all the others and these are distributed throughout

their wave functions according to the statistical probability that they will be found at any one coordinate. Hence the electrons do not avoid one another because of their mutual coulomb repulsion but tend to avoid regions of large average potential energy. Also such techniques are derived from a variational principle and their application to excited states leads to problems of orthogonality.²

Generalized variational techniques such as Hylleras or configuration-interaction expansions using a sufficiently large number of undetermined parameters give results for the upper bound to the energy to almost any desired accuracy for small atomic systems. For example, the ground state of helium has been computed to eight figures using a 39 parameter wave function³ and to ten figures using a 1078 term wave function.⁴ However, the wave functions so obtained are not uniformly convergent. This is further brought to light in the fact that the rigorous lower bound calculated with these wave functions does not usually agree with the upper bound in the last few figures. If the variational wave functions were a close approximation to the exact solution over most of the atomic configuration space one might expect better agreement between the two limits. Furthermore the number and type of correlation terms which may be included in the trial wave function are usually chosen ad-hoc. Therefore the interpretation of the resulting variational wave function for a two or three electron system does not usually lead to any real insight

into general electron-electron correlation effects. Since extensions of such expansions to atoms with many electrons must become hopelessly complex, some other techniques must be utilized to exhibit general correlation effects and give wave functions of some reliability for larger atomic systems.

In this paper we develop the method of asymptotic expansions for obtaining atomic wave functions. We look for asymptotic large Z (atomic number) wave functions of the form

$$\psi = e^{-Zh} (a_0 + a_1 Z^{-1} + a_2 Z^{-2} + \dots). \quad A$$

The energy is also expanded as a power series in Z of the form

$$E = -Z^2 (c_0^2 - Z^{-1} c_1^2 + Z^{-2} c_2^2 + \dots) \quad B$$

Insertion of A and B into the Schrodinger equation for any atom leads to a set of lower order partial differential equations for h , a_0 and a_1 . Although the energy parameters may be determinable in a self consistent manner we make use of the fact that c_0^2 and c_1^2 are known exactly for atomic systems.⁵ c_2^2 may be determined from an experimental analysis of the binding energies of the isoelectronic series of interest.

In section 2 of this paper we apply our formalism to separable atomic systems and show that truncated asymptotic expansions are exact solutions to the separable problem. In section 3 the partial differential equations for a general atomic system are solved recursively through the lowest orders.

Screening and correlation are exhibited explicitly in the resulting atomic wave functions. The correlation effects are exhibited as a sum of 2 electron correlation functions which depend on the principal quantum numbers of the electrons involved.

Asymptotic solutions of form A (naturally with different largeness parameters) have been obtained previously for a wide class of electromagnetic scattering problems⁶ and fluid dynamics problems. In those rare cases where an exact solution could be obtained by the method of separation of variables, a comparison between the asymptotic solution and the exact one has shown: 1) the leading term or terms of the asymptotic series represents the leading term or terms in the asymptotic expansion of the exact solution. 2) the asymptotic expansion including only a few terms is a very good approximation to the exact solution over most of the domain when the expansion parameter is of the order 2 or greater. From (2) we expect our asymptotic expansion to be a good approximation to the exact solution even for atoms or ions of low atomic number. That this is the case is shown by the close agreement of our results of section 4 for the angular correlation in the helium ($Z = 2$) wave function away from isolated singularity points, with those obtained from a many parameter variationally calculated wave function. From (1) we expect our asymptotic series to represent the leading terms in the asymptotic expansion in large Z of the exact solution. This is shown in part at

the end of section 4.

In section 5 we calculate some first order expectation values for the helium ground state utilizing our asymptotic expansions. Our helium wave function is shown to obey the virial theorem to first order. Magnetic susceptibilities within 5 percent of the accepted values are obtained for helium and singly ionized lithium.

In section 7 we determine by a "Matching Technique" the asymptotic expansions for Helium which are correct within a small neighborhood of the singular points. The expansions are shown to satisfy the "Cusp Condition" at the origin exactly and the one at s_{12} (inter-electron distance) = 0 to leading order. Since the wave function expansions in these regions have $\frac{\ln Z}{Z}$ terms, expectation values for operators other than the energy will include such terms in their high Z expansions. Ordinary perturbation theory expansions (7a) (7b) (7c) do not include such log terms.

2. ASYMPTOTIC SOLUTIONS FOR SEPARABLE ATOMIC SYSTEMS

The general Schrodinger equation for a system of a nucleus with charge Z surrounded by N electrons can be written in dimensionless form

$$-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \psi - \sum_{i=1}^N \frac{Z}{s_i} \psi + \left(\text{H} \sum_{i=1}^N \sum_{j>i} \frac{1}{s_{ij}} \right) \psi = E \psi \quad (1)$$

where s_i is the distance in Bohr radii of the i th electron

from the nucleus, E is the energy of the system in large Rydbergs (approximately 27.2 ev) and $\langle H \rangle$ is set equal to 0 when the electron-electron interaction is considered to be turned off and taken as 1 for the actual atomic problem.

Let us consider the case when $\langle H \rangle = 0$. The equation is then separable. That is, $\psi \approx \phi(s_1)\phi(s_2)\dots\phi(s_N)$ where $\phi(s)$ satisfies

$$-\frac{1}{2} \nabla_s^2 \phi - \frac{Z}{s} \phi - E_s \phi = 0. \quad (2)$$

The exact solution can then be represented by product wave functions of hydrogenic character. If the Pauli principle is invoked and the hydrogenic states are filled two at a time in the order of increasing energy, one builds up the periodic table with each element having its proper valence and the correct ground state symmetry properties (assuming L-S coupling to be negligible). Thus the independent electron model certainly predicts some of the more important atomic properties correctly and must in some sense represent a first approximation to the true solution. The energies of such separable systems only include the Z^2 term and can therefore be written

$$E = -Z^2 E_0 \quad \text{large Rydbergs.} \quad (3)$$

Each electron with a principal quantum number n contributes an amount $1/2n^2$ to E_0 . The exponential behavior of the wave function for an independent electron in orbital n is given by

$$\phi \approx e^{-Zs/n} \quad . \quad (4)$$

In the next section when the general problem is solved we will demand for $\langle H \rangle = 0$, $c_1^2 = 0$, $c_2^2 = 0, \dots, c_j^2 = 0$ that ψ go over to a product of separable wave functions each of which has an exponential behavior expressed by (4). In order to make complete contact with the known solution with the interaction turned off we ask that each electron for the given state of the atom or ion has the same value of n with the interaction on or off.

In the remainder of this section as a simple illustration of the asymptotic expansion technique we apply it to the separable problem (2). Substituting the formal expansion

$$\phi = e^{-Zh(s)} \sum_{j=0}^{\infty} a_j(\vec{s}) z^{-j} \quad (5)$$

and (3) into (2) and taking the gradient

$$\vec{\nabla}\phi = -Z\vec{\nabla}h + e^{-Zh} \sum_{j=0}^{\infty} z^{-j} (\vec{\nabla}a_j)$$

and Laplacian

$$\begin{aligned} \nabla^2\phi &= (\vec{\nabla}h)^2 \sum_{j=0}^{\infty} a_j z^{-j+2} - 2 \sum_{j=0}^{\infty} (\vec{\nabla}h \cdot \vec{\nabla}a_j) z^{-j+1} \\ &\quad - \nabla^2 h \sum_{j=0}^{\infty} a_j z^{-j+1} + \sum_{j=0}^{\infty} z^{-j} \nabla^2 a_j \end{aligned}$$

we obtain setting the coefficient of the z^2 term equal to 0

$$-\frac{1}{2} (\vec{\nabla}h)^2 a_0 = -E_0 a_0 . \quad (6)$$

Since $h = h(s)$, the equation can be written

$$\left(\frac{\partial h}{\partial s}\right)^2 = 2E_0$$

which admits the solution

$$h = \sqrt{2E_0} s = \alpha_0 s.$$

Setting the coefficient of the Z^1 terms = 0 gives

$$-\frac{1}{2}(\nabla h)^2 a_1 + \alpha_0 \frac{\partial a_0}{\partial s} + \frac{\alpha_0}{s} a_0 - \frac{a_0}{s} = -E_0 a_1. \quad (7)$$

The $(\nabla h)^2$ term cancels the E_0 term and we are left with homogeneous equations for a_0 of the form

$$\frac{\partial a_0}{\partial s} - \left[\frac{1}{\alpha_0} - 1 \right] \frac{a_0}{s} = 0. \quad (8)$$

Defining $\beta = \frac{1}{\alpha_0} - 1$, our result for a_0 can be written

$$a_0 = F(\theta, \phi) s^\beta$$

Setting the coefficient of the zeroth power of Z equal to 0, an inhomogeneous equation for a_1 of the form

$$\frac{\partial a_1}{\partial s} - \beta \frac{a_1}{s} = \frac{1}{2\alpha_0} \nabla^2 a_0 \quad (9)$$

results. In terms of the variable r_1 defined as $r_1 = \frac{a_1}{a_0}$, equation (9) becomes

$$\frac{\partial r_1}{\partial s} = \frac{1}{2\alpha_0 a_0} \nabla^2 a_0 \quad (9.1)$$

which for an S state ($F(\theta, \phi) = \text{const.}$) takes the form

$$\frac{dr_1}{ds} = \frac{\beta(\beta+1)}{2\alpha_0 s^2} . \quad (9.2)$$

Equation 9.2 is immediately integrated and gives

$$r_1 = -\beta(\beta+1)/2\alpha_0 s \quad (10)$$

where we have chosen the constant of integration equal to zero. Defining $r_2 = a_2/a_0$, the equation for r_2 for an S state is

$$\frac{dr_2}{ds} = \frac{1}{2\alpha_0 a_0} \nabla^2 a_1 . \quad (11)$$

Integrating we finally obtain

$$r_2 = (\beta+1)\beta^2(\beta-1)/8\alpha_0^2 s^2 . \quad (12)$$

Thus to second order in the expansion in inverse powers of Z , ϕ is of the form

$$\phi = e^{-Z\alpha_0 s} s^\beta (1 - Z^{-1} \frac{\beta(\beta+1)}{2\alpha_0 s} + Z^{-2} \frac{(\beta+1)\beta^2(\beta-1)}{8\alpha_0^2 s^2} + \dots) . \quad (13)$$

For the 1S orbital $\alpha_0 = 1$, ($\beta=0$) and the series truncates after the first term. For the 2S orbital $\alpha_0 = 1/2$ and we obtain

$$\phi = e^{-Zs/2} s(1 - 2(Zs)^{-1}) . \quad (14)$$

which is the exact 2S wave function. In the above manner we can generate all the S states for one electron systems. Choosing $F(\theta, \phi)$ in a_0 as one of the appropriate spherical

harmonics and demanding truncation, we can generate the exact wave functions for the case when the angular momentum of the system is not equal to zero. Thus we observe the well known fact that the exact solutions for the separable problem can be written as truncated asymptotic series of form (2). This simplicity arises because no interaction terms occur and the energy in the separable case can be written $-Z^2 E_0$. With interaction terms present, the energy is represented as an infinite expansion in decreasing powers of Z . This is one of the reasons no such truncation is possible in the general case.

3. ASYMPTOTIC SOLUTIONS FOR GENERAL ATOMIC SYSTEMS

We assume an asymptotic solution of equation (1) exists and is of the form

$$\psi = e^{-Zh(s_1, s_2, \dots, s_N)} \sum_{n=0}^{\infty} a_n(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_N) Z^{-n}. \quad (15)$$

The condition that our solution go over to the correct separable form with no interaction present indicates that there is no dependence of the function h on angular coordinates.

Substituting equation (15) and the energy expansion

$$E = -Z^2 \sum_{w=0}^{\infty} (-1)^w Z^{-w} c_w^2 \quad * \quad (16)$$

* In the energy expansion c_w^2 is taken as necessarily positive for $w = 0, 1$ and 2 .

into equation (1), we have after cancelling out the exponential e^{-Zh} from both sides

$$\begin{aligned}
 & -1/2 \sum_{n=0}^{\infty} \sum_{i=1}^N \left[(\vec{\nabla}_i h)^2 a_n z^{-n+2} - (2\vec{\nabla}_i h \cdot \vec{\nabla}_i a_n + (\nabla_i^2 h) a_n) z^{-n+1} \right. \\
 & \quad \left. + (\nabla_i^2 a_n) z^{-n} \right] - \sum_{n=0}^{\infty} \sum_{i=1}^N \frac{1}{s_i} a_n z^{-n+1} + \sum_{n=0}^{\infty} \sum_{i=1}^N \sum_{j>i} \frac{1}{s_{ij}} a_n z^{-n} \\
 & = -z^2 \sum_{w=0}^{\infty} (-1)^w z^{-w} c_w^2 \sum_{n=0}^{\infty} a_n z^{-n}. \tag{17}
 \end{aligned}$$

Setting the coefficient of all z^2 terms equal on both sides of the equation we obtain an eikonal equation for h of the form

$$\sum_{i=1}^N (\vec{\nabla}_i h)^2 = 2c_0^2. \tag{18}$$

Since h is not a function of angles, equation (18) can be written

$$\sum_{i=1}^N \left(\frac{\partial h}{\partial s_i} \right)^2 = 2c_0^2. \tag{18a}$$

In order that our solution go over properly for the case of no electron-electron interaction, h must be of the form

$$h = \sum_{i=1}^N \frac{s_i}{n_i} \tag{19}$$

where the i th electron is taken to be in a state with principal quantum number n_i . It then follows that each electron will

contribute an amount $1/2n^2$ to c_0^2 . Thus $c_0^2 = E_0$ and is therefore determined since E_0 is known. For example in the case of a filled shell atom whose outer shell has a principal quantum number N ,

$$E_0 = 2 \sum_{n=1}^N 1/2n^2 \sum_{\ell=0}^{n-1} (2\ell+1).$$

In more conventional perturbation theory techniques the electron position coordinates in equation (1) are all multiplied by Z and this results in a $1/Z$ appearing as the perturbation parameter multiplying the $1/s_{ij}$ term. It then follows immediately that the leading term of the energy expansion is the unperturbed energy obtained with $1/Z$ equal to 0 which is just the separable energy $-Z^2 E_0$.

Equating coefficients of Z^1 terms on both sides of equation (17) we obtain

$$\sum_{i=1}^N [-1/2(\vec{\nabla}_i h)^2 a_1 + \vec{\nabla}_i h \cdot \vec{\nabla}_i a_0 + 1/2(\nabla_i^2 h)a_0 - 1/s_i a_0] = -c_0^2 a_1 + c_1^2 a_0 . \quad (20)$$

From equation 18, it follows that the coefficients of the a_1 terms on both sides of equation (20) are equal. The resulting equation for a_0 is therefore

$$\sum_{i=1}^N [\frac{1}{n_i} \frac{\partial a_0}{\partial s_i} + (1/n_i - 1)1/s_i a_0] = c_1^2 a_0 . \quad (21)$$

Equation 21 admits the general solution

$$a_0 = J_0 \prod_{i=1}^N s_i^{-\omega_i} e^{\lambda_i s_i} \quad (22)$$

where

$$\omega_i = l - n_i$$

$$\lambda_i = n_i c_l^2 / N$$

and J_0 is an arbitrary function of angles and of the differences formed by taking the radial coordinates of any two electrons, multiplying each by its principal quantum number and then subtracting one from the other. Choosing J_0 as a product of the appropriate spherical harmonic functions of the angular coordinates of those electrons not in S states, our solution goes over correctly for the separable case. From the above form of the λ_i 's, it follows that in any given ion or atom the shielding factor for any electron is approximately proportional to its average distance from the nucleus with the interaction turned off.

Equating coefficients of the zeroth power terms, we obtain an inhomogeneous equation for a_1 of the form

$$\sum_{i=1}^N \left(\frac{1}{n_i} \frac{\partial a_1}{\partial s_i} + \left(\frac{1}{n_i} - 1 \right) \frac{1}{s_i} a_1 \right) - c_l^2 a_1 = \\ - \bigcircledH a_0 \sum_{i=1}^N \sum_{j>i} \frac{1}{s_{ij}} + \frac{1}{2} \sum_{i=1}^N \nabla_i^2 a_0 - c_2^2 a_0 . \quad (23)$$

Making the substitution $a_1 = r_1 a_0$ and noting that both functions a_0 and a_1 satisfy the same homogeneous equation, we find equation 23 reduces to

$$\sum_{i=1}^N \frac{1}{n_i} \frac{\partial r_1}{\partial s_i} = - \textcircled{H} \sum_{i=1}^N \sum_{j>i} \frac{1}{s_{ij}} + \frac{1}{2a_0} \sum_{i=1}^N \nabla_i^2 a_0 - c_2^2. \quad (24)$$

The solution to equation 24 can be written

$$r_1 = \textcircled{H} \sum_{i=1}^N \sum_{j>i} c_{ij} + \frac{1}{2} \sum_{i=1}^N n_i \int \frac{\nabla_i^2 a_0}{a_0} ds_i - \sum_{i=1}^N \frac{c_2^2}{N} n_i s_i \quad (25)$$

where c_{ij} is the solution of

$$\frac{1}{n_i} \frac{\partial c}{\partial s_i} + \frac{1}{n_j} \frac{\partial c}{\partial s_j} = - \frac{1}{s_{ij}} \quad (26)$$

subject to the boundary condition that as either s_i or s_j goes to infinity or zero with the other held fixed, c_{ij} goes to zero. This condition follows since c_{ij} represents the direct correlation term in our first order solution. As the electrons go infinitely far apart from one another, the electron-electron interaction contribution to the wave function goes to zero. The solution of equation 26 is shown by standard techniques⁸ to be of the form

$$c_{ij} = \frac{-n_j n_i}{Q_{ij}} \log \left(\frac{s_{ij} Q_{ij} + (n_j - D_{ij}) n_i s_i + (n_i - D_{ij}) n_j s_j}{A_{ij}} \right) \quad (27)$$

where

θ_{ij} is the angle subtended at the nucleus between electrons i and j , $D_{ij} = \cos \theta_{ij}$,

$$Q_{ij} = \sqrt{n_i^2 + n_j^2 - 2D_{ij}n_i n_j}, \text{ and}$$

$$A_{ij} = (Q_{ij} + n_j - D_{ij}n_i)(s_i - (n_j/n_i)s_j) \text{ for } n_j s_j < n_i s_i.$$

It is obvious from 27 that c_{ij} depends only on the ratio s_i/s_j and the angle between the electrons.

It should be noted that in the analysis of this section we have tacitly assumed that no non-uniformities occur in performing the two limiting procedures $(\text{H}) \rightarrow 0$, $Z \rightarrow \infty$.

4. ASYMPTOTIC GROUND STATE SOLUTIONS FOR 2 ELECTRON ATOMS

The ground state of a two electron atomic system consists of a $1s^2$ configuration. Since both electrons are in orbitals with a principal quantum number of 1, we obtain

$$\omega_1 = \omega_2 = 0$$

$$\lambda_1 = \lambda_2 = \lambda = c_1^2/2,$$

and equation 22 for a_0 gives

$$a_0 = e^{\lambda(s_1+s_2)}. \quad (28)$$

Operating on a_0 with the Laplacian we obtain

$$\frac{\nabla_i^2 a_0}{a_0} = \frac{2\lambda}{s_i} + \lambda^2 .$$

Performing the integration in equation 25 we are led to the result

$$r_1 = c_{12}(1,1) + \lambda \log s_1 s_2 + 1/2(\lambda^2 - c_2^2)(s_1 + s_2) \quad (29)$$

where $c_{ij}(n_i, n_j)$ refers to the correlation function when electron i is in an orbital with principal quantum number n_i and electron j is in an orbital with principal quantum number n_j . Equation 27 for $n_i = n_j = 1$ gives

$$c_{12}(1,1) = -\frac{1}{2d} \log \left(\frac{s_{12} + d(s_1 + s_2)}{(1+d)|s_1 - s_2|} \right) \quad (30)$$

with

$$d = (1 - D_{12})/2 \quad \text{and} \quad D_{12} = \cos \theta_{12}.$$

The isoelectronic energy expansion is well known for the case of 2 electron atomic systems.⁹ In terms of large rydbergs we observe that $c_1^2 = .625$ and $c_2^2 = .15765$. Using these values we obtain $\lambda = .3125$ and the coefficient β of the $s_1 + s_2$ term is $- .03$. The first order asymptotic wave function for a 2 electron atomic system is then

$$\psi_1 = e^{-(Z-\lambda)(s_1+s_2)} [1 + Z^{-1}(c_{12}(1,1) + \lambda \log(s_1 s_2) + \beta(s_1 + s_2))]. \quad (31)$$

Since the value .3125 for our shielding parameter λ is

exactly the value found by performing a variational calculation on a simple exponential product wave function, the leading term of ψ_1 is already well known. On graph 1, $c_{12}(1,1)$ is plotted as a function of x ($x=s_2/s_1$) for $\theta_{12} = 0^\circ$. This is the case when the two electrons are both on the same side of the nucleus and lie on a straight line which passes through it. We observe that c_{12} goes to zero as the electrons go infinitely far apart. As the electrons come near one another, c_{12} becomes more and more negative leading to a smaller value for ψ_1 and therefore to a decreased probability of finding the electrons close together. These are the correlation effects one expects physically.

In point of fact, c_{12} diverges logarithmically at $s_1 = s_2$. For the case of $\theta_{12} = 0^\circ$ the divergence is stronger and a first order pole occurs. This type of singularity at a point about which the asymptotic expansion changes character is common to many asymptotic solutions. For example the WKB asymptotic solution of the simple harmonic oscillator diverges in the neighborhood of the classical turning point. The asymptotic solution also changes character about this point. Often one can obtain by a stretching technique an accurate non-divergent asymptotic solution in the transition region where the original asymptotic solutions diverged. For the harmonic oscillator such a stretched solution is the Airy function. Simply stated, such singularity phenomena occur because the postulated form of the asymptotic expansion is not

adequate to represent the asymptotic expansion of the true solution in this region due to problems of non-uniform convergence. This will be discussed further in sections 6 and 7 when we obtain the asymptotic expansion in the n.b.h. of singular points. In another sense one may sometimes think of the occurrence of such singularities as due to our conversion of a problem involving a second order partial differential equation to one where a set of first order equations are solved recursively. Somewhere in the process a boundary condition may be lost. In trying to recover the correct boundary value the asymptotic solution overshoots the mark. Thus we do not expect our asymptotic expansion to be valid in some neighborhood of the points $s_1 = s_2$. However from the plots of our correlation function as a function of x as shown in figure 2 for various angles, we expect radial correlation to be a general property of the helium ground state system. That is, one should observe a reduced probability of finding 2 electrons having the same value of the radial coordinate. Strong radial correlation effects in the helium wave function have been discussed elsewhere.¹⁰ We also observe from figure 2 that the correlation effect for any value of x decreases with decreasing D_{12} and therefore with increasing s_{12} as expected.

In figure 3, we compare ψ_1 for helium and doubly ionized beryllium for the case $s_1 = .5$, $\theta_{12} = 0^\circ$. It is physically unreasonable that the true helium wave function

becomes negative in the neighborhood of $s_{12} = 0$. We note from the figure that this phenomenon will occur much further from the point $s_1 = s_2$ in the case of helium than for doubly ionized beryllium. Therefore it is immediately obvious that our solutions become applicable closer to $s_1 = s_2$ as Z becomes larger. As Z goes toward infinity our solution ψ_1 will become applicable over almost all configuration space.

It should also be pointed out that 1S orbitals give rise to a logarithmic singularity when either electron goes into the nucleus. The region in the neighborhood of the nucleus in which this effect is large is small, even for $Z = 2$. It is of the order of .3 bohr radii for this case. A non-divergent asymptotic solution which is correct in the neighborhood of the origin can be found by a stretching technique. As our electrons go an infinite distance away from the nucleus, the usual non-convergence problems arise in the wave function. Since this domain will not be of interest in computing expectation values we do not trouble ourselves about it here. To avoid this problem one has to use a density matrix formulation of the problem.

In figure 4, we plot ψ_1 as a function of s_2 for the case $s_1 = 2, \theta_{12} = 0^\circ$. In the same figure we plot the leading term of ψ_1 which is just a product of screened exponentials. We refer to this term as ψ_0 . Note that ψ_1 becomes less than ψ_0 in the neighborhood of $s_{12} = 0$ and larger than ψ_0 as the distance between electrons increases. Because of

the compensating effects in the different regions, when a correct asymptotic description of the wave function in the immediate neighborhood of $s_{12} = 0$ and the origin is used in conjunction with our asymptotic solution which is valid everywhere else, we expect the correct normalization constant multiplying ψ_1 will be only slightly changed from the normalization constant for ψ_0 . Assuming ψ_1 to have the same normalization factor as ψ_0 , we have calculated a correlation correction factor which is just the ratio of the two wave functions. In figure 6, we compare our results with those of Gilbert¹¹ who obtained this correction factor utilizing a many parameter variationally determined Hylleras type wave function. In these plots we are holding the radial coordinates s_1 and s_2 fixed while changing the distance between the electrons by varying the angle subtended at the nucleus by the two electrons (for $\theta_{12} = 0^\circ$, $s_{12} = s_1 - s_2$; for $\theta_{12} = 180^\circ$, $s_{12} = s_1 + s_2$.) We expect physically the greatest correlation to occur for θ_{12} smallest. This is borne out by the curves. In the case of the $s_1 = 2$, $s_2 = 3$ case we run into the s_1 approximately equal to s_2 distortion phenomena. Our correlation factor is too low for small angles as expected. However outside of this region our results agree quite well with Gilbert's and if we used the correct normalization constant for ψ_1 we expect that the agreement would be improved.

For large s_1 and s_2 it is known that the exact solution

for helium has an exponential behavior given by

$$\psi \sim e^{-\sqrt{-E}(s_1+s_2)} \quad (32)$$

where E is the energy eigenvalue. Putting in the energy expansion for E in terms of the C 's and expanding the exponential to first order in powers of $1/Z$ we obtain for Z large

$$\psi \sim e^{-(Z-\lambda)(s_1+s_2)} [1 + Z^{-1}(\lambda^2 - C_2^2)(s_1+s_2)/2].$$

Comparing our asymptotic expansion, equation 29, with this, we observe that it gives the correct high Z asymptotic expansion of the exponential part of the exact wave function for the above case.

5. EXPECTATION VALUES FOR 2 ELECTRON ATOMIC SYSTEMS

In the previous section we investigated the properties of the asymptotic helium wave function and found certain unphysical logarithmic divergences which occur at $s_i = 0$, and $s_i = s_j$. However these inaccuracies in our wave function have little effect on the expectation values of those operators which are relatively insensitive to the values of the wave function in the neighborhood of these points. Such operators as s_{12}^2 , s_{12} , $1/2(s_1^2 + s_2^2)$, $1/2(s_1 + s_2)$, and $1/2(1/s_1 + 1/s_2)$ fall into the above class. Expectation value computations to first order in $1/Z$ were performed for these operators and our results and a comparison with the "exact" results of Pekeris⁴ for helium and singly ionized lithium are given in

the tables below. All values are given in atomic units.

Table 1. Helium Expectation Values*

Operator	Expectation Values	
	Pekeris	Asymptotic
$1/2(s_1^2 + s_2^2)$	1.193	1.186
$1/2(s_1 + s_2)$.9295	.9453
$1/2(1/s_1 + 1/s_2)$	1.68832	1.68750
s_{12}^2	2.516	2.600
s_{12}	1.422	1.547

Table 2. Lithium⁺ Expectation Values

Operator	Expectation Values	
	Pekeris	Asymptotic
$1/2(s_1^2 + s_2^2)$.4463	.4624
$1/2(s_1 + s_2)$.5728	5868
$1/2(1/s_1 + 1/s_2)$	2.6879	2.6875
s_{12}^2	.9271	.9925
s_{12}	.8623	.9307

Our calculations necessitated one numerical double integration over a finite domain for each expectation value. These integrations were performed on the 7094 computer using

* Pekeris' data is originally given to 10 figures.

a trapezoidal rule numerical integration scheme . Our numerical integration results are generally good to 4 figures. For the calculation of the nuclear magnetic shielding constant, $1/2(1/s_1 + 1/s_2)$, the results were extrapolated to six significant figures. The value of 1.68750 for this expectation value shows that ψ_1 satisfies the virial theorem to first order in $1/Z$.¹² Our result for the diamagnetic susceptibility, $1/2(s_1^2 + s_2^2)$, of helium is within 1/2 per cent of the exact one.

In performing our computations we form the product $\psi_1^* O \psi_1$ where O is the operator under consideration and calculate

$$\bar{O} = \frac{\int dV \psi_1^* O \psi_1}{\int dV \psi_1^* \psi_1} \quad (33)$$

to first order in $1/Z$. When performing integrations not involving terms dependent on s_{12} or D_{12} it is convenient to choose

$$\int dV = (4\pi)^2 \int_0^\infty \int_0^\infty ds_1 ds_2 s_1^2 s_2^2.$$

For integrations involving correlation terms we take

$$\int dV = 2\pi^2 \int_0^\infty ds \int_0^s du u \int_0^u dt (s^2 - t^2) \quad (34)$$

where $s = s_1 + s_2$, $t = s_1 - s_2$ and $u = s_{12}$. For operators of the form $O_j = 1/2(s_1^j + s_2^j)$, the $\lambda(\log s_1 + \log s_2)$ term is evaluated utilizing

$$\int_0^\infty dx e^{-kx} x^j \log x = \frac{j! [\psi(j+1) - \log k]}{k^{j+1}} \quad (35)$$

where

$$\psi(j+1) = \int_0^\infty dy e^{-y} y^j \log y = \frac{d}{dq} \log \Gamma(q)|_{q=j+1}$$

and has been evaluated elsewhere.¹⁴ Making a change of variables in the integral containing the C_{12} term

$$u \rightarrow a = u/s$$

$$t \rightarrow y = (1-(u^2-t^2)^{1/2}/((s^2-t^2)^{1/2}a))^{1/2}$$

the s integration can be performed separately and what remains is a double integration over a finite domain of the form

$$CJ = 2 \int_0^1 da a(1-a^2) \int_0^1 dy f_j(y,a) (\log w(y,a) - \log y) \quad (37)$$

with

$$w = \left(\frac{(1-(1-y^2)a)(2-y^2)}{(1+(1-y^2)a)} \right)^{1/2}$$

and

$$f_j(y,a) = (o_j/s^j)/((1-(1-y^2)^2 a^2)^{5/2} (2-y^2)^{1/2}).$$

The $\log y$ term in equation 37 can be evaluated numerically by rewriting it

$$\int_0^1 dy f_j(y,a) \log y = -f_j(0,a) + \int_0^1 dy (f_j(y,a) - f_j(0,a)) \log y. \quad (38)$$

We obtain finally

$$\overline{O}_j = \frac{(2+j)!}{2(2z)^j} \left(1 + \frac{1}{Z} \left[(j + 2[\psi(3+j) - \psi(3)]) \right. \right. \\ \left. \left. + \frac{1}{2} \frac{5!}{2^5} \text{co} - \frac{(6+j-1)!}{(2+j)!2^5} CJ \right] + O(1/z^2) \right). \quad (39)$$

Similarly expectation values of operators s_{12}^{-j} are found to be of the form

$$\overline{s_{12}^{-j}} = \frac{(j+5)!}{(2z)^j 2^5} \left(\frac{1}{j+3} - \frac{1}{3(j+5)} \right) \left[1 + \right. \\ \left. \frac{1}{Z} \left(\lambda (j + 4[\psi(6+j) - \psi(3)] - 2 \log 4 \right. \right. \\ \left. \left. + \frac{2 I_j}{\frac{1}{3+j} - \frac{1}{3(5+j)}} \right) + \frac{5!}{2^5} \text{co} - \frac{\text{CS12J}}{\frac{1}{3+j} - \frac{1}{3(5+j)}} \right) \right] \quad (40)$$

where CS12J has the same form as CJ except that O_j/s_j^j is replaced by a^j in the integrand and we have taken

$$I_j = \int_0^1 d\beta \beta^{2+j} \int_0^1 d\alpha (1-\alpha^2 \beta^2) \log(1-\alpha^2 \beta^2)$$

which can be evaluated analytically in terms of standard quadratures.

6. Technique of "Matched Asymptotic Expansions"

The asymptotic expansion for the ground state of helium has been found to diverge at certain singular points. We shall

now discuss the technique of "matched asymptotic expansions" (stretching) for obtaining an accurate non-divergent asymptotic solution in the neighborhood of any one of the singular points.

Let us consider the exact solution $\psi(Z; x_1, x_2, x_3)$ of our many body problem with Hamiltonian H and a two term formal asymptotic expansion ψ_1 obtained by the methods of section 3. Suppose we want to determine the asymptotic expansion of ψ in the neighborhood of the point $x_1 = 0$ where ψ_1 blows up unphysically. Now although it has not been generally proven, we take

$$\tilde{\psi}(Z \text{ large}) \rightarrow \psi_1$$

where the wiggle over the ψ indicates "the expansion of" and the arguments inside the parenthesis indicate the limiting procedures for obtaining the expansion. If more than 1 limiting process is involved, the one furthest to the right is the first to be performed. Now when we evaluate ψ_1 as $x_1 \rightarrow 0$ we are performing the limit process

$$\tilde{\psi}(x_1 \rightarrow 0, Z \text{ large}) \rightarrow \psi_1(x_1 \rightarrow 0) \rightarrow \text{divergence}.$$

However near the point $x_1 = 0$ for Z large but finite we really want to evaluate

$$\tilde{\psi}(Z \text{ large}, x_1 \rightarrow 0)$$

where

$$\tilde{\psi}(Z \text{ large}, x_1 \rightarrow 0) \neq \tilde{\psi}(x_1 \rightarrow 0, Z \text{ large}) \approx \psi_1(x_1 \rightarrow 0).$$

Let us consider a transformation of variables where we rewrite our operator H in terms of a new stretched variable ξ_1 . That is

$$x_1 \rightarrow \xi_1 = z^j x_1 \quad \text{where } j > 0 \quad (j \text{ as yet otherwise unspecified})$$

$$H(z; x_1, x_2, x_3) \rightarrow \bar{H}(z; \xi_1, x_2, x_3).$$

Such a change of variables guarantees that when considering the z dependence of terms in \bar{H} :

A. Terms in H which go as $x_1^k (k > 0)$ will be small when expressed in \bar{H} . On the other hand $k < 0$ terms will be large. [Note that for x_1 small we expect terms $\sim x_1^k (k > 0)$ in H to be small.]

B. Terms $\frac{\partial \psi}{\partial x_1}$ in H will be of magnitude $z^j \frac{\partial \psi}{\partial \xi_1}$ in \bar{H} .

This implies that if we look for a solution of the form $\psi \approx \phi \exp f(z, \xi_1, x_2, x_3)$, the leading term of $\frac{\partial \phi}{\partial x_1}$ in the neighborhood of $x_1 \approx 0$ will be of magnitude z^j greater than the leading terms of $\frac{\partial \phi}{\partial x_2}$ or $\frac{\partial \phi}{\partial x_3}$ in this region when each is reexpressed as a function of ξ_1 , x_2 and x_3 . [Note again that for x_1 small we expect our boundary layer solution to vary more rapidly with x_1 (have a larger partial derivative) than in the case of the asymptotic solution away from the singular point. The proper stretching accomplishes this].

Thus we see that stretching is a way of ordering the terms in H in the n.b.h. of $x_1 \approx 0$. When considering

\bar{H} , this ordering is expressed simply by the dependence of the various terms on a single parameter Z . We can again look for solutions of the standard asymptotic form (15). The resulting system of partial differential equations to be solved is naturally simpler than the original problem. However because of our ordering the equations are only applicable near $x_1 = 0$.

Let us call the formal two term asymptotic solution to the stretched problem $-\bar{\psi}_1(Z; \xi_1, x_2, x_3)$. We expect that if j has been chosen correctly that $\bar{\psi}_1$ is an asymptotic expansion of ψ which is valid for Z large, ξ_1 small. Since $\xi_1 = Z^j x_1$, the solution

$$\bar{\psi}_1(\xi_1 \text{ large})$$

corresponds to $\tilde{\psi}(x_1 \text{ small}, Z \text{ large})$ and therefore we expect

$$\bar{\psi}_1(\xi_1 \text{ large}) \rightarrow \psi_1(x_1 \text{ small}).$$

This is called the "matching condition". Only the correct value of j will allow this condition to be satisfied even though certain constants and/or functions in $\bar{\psi}_1$ are determined from it. Once it is satisfied, the solution $\bar{\psi}_1$ for ξ_1 small obviously corresponds to $\tilde{\psi}(Z \text{ large}, x_1 \text{ small})$ and is therefore the desired asymptotic expansion in the neighborhood of $x_1 \approx 0$. Another important consideration in determining the requisite value of j is that we expect at least some of the operators present in the P.D.E. for r_1 of the original asymptotic expansion will also be present in

the P.D.E. for m_1 . In addition we also expect some second order partial derivative terms to appear in the equation for m_1 . For the case of ψ_1 becoming divergent at $x_1 = 0$, $x_2 = 0$ it may be necessary to perform different stretchings on variables x_1 and x_2 but essentially the same considerations go through for understanding the "matching principle." From physical considerations one can usually ascertain whether ψ varies more rapidly (its partial derivative is greater) with respect to one variable than the other in the neighborhood of the singular point. It is then the former variable which receives the greater stretching.

In the foregoing we have introduced the idea of stretching and have indicated how the matching principle is fulfilled. We now state more explicitly the form of the matching principle⁽¹⁵⁾ utilized in this paper which is

"The two term expansion of ψ_1 (when it is expressed in terms of stretched variables) in powers of $1/Z$ = the two term expansion of $\bar{\psi}_1$ (when it is expressed in terms of ordinary variables) in powers of $1/Z$."

For the case that ψ_1 is singular at $x_1 = 0$, defining

$$\underline{\psi}_1(Z; \xi_1, x_2, x_3) = \psi_1\left(Z; \frac{\xi_1}{Z^j}, x_2, x_3\right),$$

$$\underline{\psi}_{1E} = \underline{\psi}_1(\text{EXPANDED FOR } Z \text{ LARGE, KEEPING 2 LARGEST ORDERS}),$$

$$\underline{\bar{\psi}}_1(Z; x_1, x_2, x_3) = \bar{\psi}_1(Z; Z^j x_1, x_2, x_3),$$

and

$$\underline{\bar{\psi}}_{1E} = \bar{\psi}_1(\text{EXPANDED FOR } Z \text{ LARGE, KEEPING 2 HIGHEST ORDERS})$$

the "matching principle" asserts

$$\overline{\psi}_{1E} \underset{\sim}{=} \psi_{1E}^*$$

7. SOLUTIONS IN THE NEIGHBORHOOD OF SINGULAR POINTS

Before we begin our investigation, we would like to summarize the notation* used in this section.

ψ_1 , The helium ground state asymptotic wave function obtained in section 4 is written in terms of ordinary variables as

$$\psi_1 = e^{-Zh} [1 + \frac{1}{Z} r_1].$$

ψ_1 , When ψ_1 above is rewritten in terms of the stretched variables associated with the singular point under investigation it is denoted by

$$\psi_1 = e^{-Zh} [1 + \frac{1}{Z} \tilde{r}_1]$$

where \tilde{r}_1 is written in terms of d_1 . In general a wiggle under a symbol means it is being reexpressed in terms of unnatural variables.

ψ_{1E} , $\tilde{\psi}_{1E}$ is the expansion of ψ_1 in powers of $1/Z$, keeping only the two leading terms.

r_{1E} , \tilde{r}_{1E} is the expansion of r_1 in powers of $1/Z$, keeping only the leading term.

$\overline{\psi}$, The asymptotic solution of the stretched problem in terms of stretched variables is denoted by

$$\overline{\psi} = e^{-Zh'} [1 + \frac{m_1}{Z}]$$

* In region Ib, these definitions are modified slightly.

where $h' = h$ for regions I and they are not equivalent in regions II.

$\tilde{\psi}$, When $\tilde{\psi}$ is written in terms of unstretched variables, we denote it by

$$\tilde{\psi} = e^{-Zh'} [1 + \frac{m_1}{Z}].$$

$\tilde{\psi}_E$, $\tilde{\psi}_E$ is the expansion of $\tilde{\psi}$ in powers of $1/Z$, keeping only the two leading terms.

m_{1E} , m_{1E} is the expansion of m_1 in powers of $1/Z$, keeping only the leading term.

Our helium ground state asymptotic solution ψ_1 diverges in the following regions:

Ia. ($t=0, u \neq 0$)

Ib. ($u=0, s \neq 0$)

IIa. ($s_1=0, s_2 \neq 0$)

IIb. ($s_1=0, s_2=0$)

To find the correct asymptotic solutions for regions I we rewrite the 2 electron Schrodinger equation in coordinates s, t, u as

$$\begin{aligned} & u(s^2 - t^2) \left(\frac{\partial^2 \psi}{\partial s^2} + \frac{\partial^2 \psi}{\partial u^2} + \frac{\partial^2 \psi}{\partial t^2} \right) + 2s(u^2 - t^2) \frac{\partial^2 \psi}{\partial s \partial u} \\ & + 2t(s^2 - u^2) \frac{\partial^2 \psi}{\partial u \partial t} + 4su \frac{\partial \psi}{\partial s} + 2(s^2 - t^2) \frac{\partial \psi}{\partial u} - 4ut \frac{\partial \psi}{\partial t} \\ & + 4Zsu\psi - (s^2 - t^2)\psi + Eu(s^2 - t^2)\psi = 0 \end{aligned} \quad (41)$$

with E given as before by (16). Regions Ia and Ib

are considered removed from the origin. Thus we do not have to consider any stretching in s and expect that the exponential dependence on s (shielding effect) will be the same for the Ia and Ib solutions as for the original asymptotic solution. Therefore we look in regions Ia and Ib for stretched solutions of the form

$$\bar{\psi} = e^{-(Z-\lambda)s} \left[1 + \frac{m_1}{Z} + \frac{m_2}{Z^2} + \dots \right].^* \quad (42)$$

In appendix I we have substituted the above into equation 41 and have kept terms through order $1/Z$ considering $\psi = \psi(s, t, u)$. Certain terms automatically cancel one another in equation Al. These terms are enclosed in boxes and need not be considered further. Now consider the general double stretching

$$\xi = Z^k t$$

$$\gamma = Z^j u.$$

Under each term of equation Al we express the order of that term in Z when considered as a function of ξ , γ , and Z in terms of the j , k of the transformation. For the case $j = 0$, $k = 0$ (no stretching) the largest terms are of order Z^0 and equating them equal to 0 we obtain

$$\begin{aligned} & us^2 [\lambda^2 - 2 \frac{\partial m_1}{\partial s}] - ut^2 [\lambda^2 - 2 \frac{\partial m_1}{\partial s}] \\ & - 2s[u^2 - t^2] \frac{\partial m_1}{\partial u} + 4\lambda su - s^2 + t^2 - c_2^2 [us^2 - ut^2] = 0. \end{aligned} \quad (43)$$

It is a simple matter to show that this equation is satisfied

* $\bar{\psi}$ here is taken as the general expansion, but only terms through m_1 will be of importance in satisfying the "matching theorem".

by the r_1 (equation 29) of our original asymptotic expansion.

We will indicate this as expansion A. The terms in equation Al entering the leading equation for expansion A (equation 42) are indicated by writing an A above the term. Since there is one term, $-s^2$ in Al which is independent of j and k , it is necessary that other terms in Al which depend on j and k are also of order Z^0 if we are to be able to equate the coefficient of this power of Z equal to 0. For the region Ia no stretching is required on the s_{12} variable and $j = 0, k = \frac{1}{2}$ are the proper values of j and k .

For the case $j = 1, k = \frac{1}{2}$ we obtain the expansion in region Ib. For both cases the P.D.E. to be satisfied by m_1 is found by setting the coefficient of the Z^0 terms equal to zero. The terms entering the equation for m_1 in region Ia have a Ia written above them in eq. Al. Similarly those entering in region Ib have a Ib written above them. Note that of the four differential operator terms present in A, two are present in Ia and one is present in Ib. If for example we had chosen $j = 1, k = 1$ as the proper stretching in Ib, none of the differential operator terms present in A would have entered the equation for m_1 . Needless to say, pursuance of the $j = 1, k = 1$ solution for m_1 would have indicated that no match with the asymptotic expansion A was possible.

We now write down the P.D.E. for m_1 in region Ia as

$$\frac{\partial^2 m_1}{\partial \xi^2} - 2 \frac{\partial m_1}{\partial s} - 2 u/s \frac{\partial m_1}{\partial u} = \frac{1}{u} - \frac{4\lambda}{s} - [\lambda^2 - c_2^2] \quad (44)$$

where $\xi = Z^{1/2}t$. Now we have r_1 of expansion A which can be written

$$r_1(s, t, u) = [\lambda \log(\frac{s^2 - t^2}{4}) + \frac{1}{2}[\lambda^2 - c_2^2]s - \frac{1}{2d} \log(\frac{u + ds}{(1+d)|t|})]^{1/2} \quad (45)$$

where $d = [\frac{u^2 - t^2}{s^2 - t^2}]^{1/2}$. This is immediately seen by referring to equation 29 and rewriting it in terms of the variables s , t and u . Following our prescription at the end of section 6

$$\begin{aligned} r_1 &= [\lambda \log \frac{s^2}{4} [1 - \frac{\xi^2}{Zs^2}] + \frac{1}{2}[\lambda^2 - c_2^2]s \\ &\quad - \frac{1}{2d} \log(\frac{s_{12} + d_1 s}{(1+d_1)|\xi/Z^{1/2}|})]^{1/2} \end{aligned}$$

with

$$d_1(Z; \xi, s, u) = d(Z; \frac{\xi}{Z^{1/2}}, s, u) = \frac{u}{s} \left[\frac{1 - \frac{\xi^2}{Zu^2}}{1 - \frac{\xi^2}{Zs^2}} \right]^{1/2}.$$

Expanding for large Z

$$\frac{1}{2d_1} \approx \frac{1}{2} \left(\frac{s}{u} \right) \left[1 + \frac{1}{2Z} \left(\frac{1}{u^2} - \frac{1}{s^2} \right) + O\left(\frac{1}{Z^2}\right) \right]$$

$$d_1 s \approx u \left[1 + \frac{\xi^2}{2Z} \left(\frac{1}{s^2} - \frac{1}{u^2} \right) + O\left(\frac{1}{Z^2}\right) \right]$$

we obtain

$$\tilde{r}_{1E} \sim \left[\lambda \log \frac{s^2}{4} + \frac{1}{2} [\lambda^2 - c_2^2] s + \frac{s}{2u} [\log \frac{|\xi|}{Z^{1/2}} - (\log 2u - \log(1 + u/s))] \right] + O(\frac{\log Z}{Z}). \quad (46)$$

In order to satisfy the matching principle m_{1E} obtained from m_1 of equation 44 must be equal to \tilde{r}_{1E} given by equation 46. Choosing

$$m_1 = \lambda \log s^2 + \frac{1}{2} [\lambda^2 - c_2^2] s - \frac{s}{2u} [\log 2u - \log(1 + u/s) + M_1] \quad (47)$$

and substituting into equation 46 we find M_1 satisfies the heat flow equation

$$\frac{\partial^2 M_1}{\partial \xi^2} = 2 \frac{\partial M_1}{\partial s}. \quad (48)$$

To complete the match we expect for large ξ

$$M_1 = -\log \xi + \sum a_j(s) \xi^{-j} \quad \text{with } a_{-1} = 0. \quad (49)$$

Substituting 49 into 48 we obtain

$$\frac{1}{s^2} + \sum_{j=2} (j-2)(j-1)a_{j-2}\xi^{-j} - \sum_j 2 \frac{\partial a_j}{\partial s} \xi^{-j} = 0. \quad (50)$$

Thus $a_0 = \text{constant}$. Since ψ must be even in t and therefore in ξ we next set the coefficients of ξ^{-2} in (50) equal to 0 obtaining

$$-2 \frac{\partial a_2}{\partial s} + 1 = 0 \quad (51)$$

which has the solution

$$a_2 = \frac{1}{2} s. \quad (52)$$

For higher values of j we find recursively

$$a_j = \frac{(j-2)(j-1)}{2} \int ds a_{j-2}. \quad (53)$$

Defining $w = s/\xi^2$ we observe that for ξ large, w small, we can write

$$M_1 = -\log \xi + a_0 + \frac{w}{2} + \frac{3}{4} w^2 + \dots . \quad (54)$$

Therefore we look for a general solution of (48) of the form

$$M_1 = -\log \xi + a_0 + \phi(w) \quad (55)$$

with

$$\phi(w) \approx w/2 + 3/4 w^2 + \dots \quad (55a)$$

for w large. Substituting we obtain

$$\frac{d^2\phi}{dw^2} + \frac{1}{2} [\frac{3}{w} - \frac{1}{w^2}] \frac{d\phi}{dw} = -\frac{1}{4w^2} \quad (56)$$

which has the general solution

$$\phi = C_1 \int dw w^{-3/2} e^{-\frac{1}{2w}} - \frac{1}{4} \int dw w^{-3/2} e^{-\frac{1}{2w}} \int dw: \frac{e^{-\frac{1}{2w}}}{w^{1/2}} . \quad (57)$$

substituting $V = \frac{1}{2w}$ we obtain

$$\phi = -C_1 \int \frac{dV}{V^{1/2}} e^{-V} - \frac{1}{4} \int \frac{dV}{V^{1/2}} e^{-V} \int^V \frac{du}{u^{3/2}} e^u . \quad (58)$$

Now the homogeneous term would admit odd powers of ξ which is unphysical. Therefore we set $c_1 = 0$. Now we write our solution

$$\phi = -\frac{1}{4} \int \frac{dv}{v^{1/2}} e^{-v} g(v) \quad (59a)$$

with

$$g(v) = \int_{-\infty}^v \frac{du}{u^{3/2}} e^u . \quad (59b)$$

The lower limit on integral 59b has been chosen so that no contributions from partial integrations will result from it. For v large, w small we partially integrate to higher negative powers of v giving

$$g(v) \approx e^v \left[\frac{1}{v^{3/2}} + \frac{3}{2} \frac{1}{v^{5/2}} + \frac{3 \cdot 5}{2^2} \frac{1}{v^{7/2}} + \dots \right] \quad (60)$$

which results in

$$\phi(v) \approx \frac{1}{4} \sum_{n=1} \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{(2^{n-1})_n} \frac{1}{v^n} \quad (61)$$

which gives as its leading terms

$$\phi(v) \approx \frac{1}{4v} + \frac{3}{16v^2} + \dots = \frac{w}{2} + \frac{3}{4} w^2 + \dots . \quad (62)$$

which is the previously obtained expansion (55a).

We can now write

$$m_1 = \lambda \log s^2 + \frac{1}{2} [\lambda^2 - c_2^2] s - \frac{s}{2u} [\log 2u - \log(1+u/s) - \log \xi + a_0 + \phi(w)] . \quad (63)$$

We rewrite $w = s/\xi^2 = s/z_t^2$. Thus for Z large w is small and $\phi(w)$ is given by (62). Therefore

$$\begin{aligned} m_1 &\approx \lambda \log s^2 + \frac{1}{2} [\lambda^2 - c_2^2] s - \frac{s}{2u[\log 2u - \log(1+u/s) - \log \xi + a_0]} \\ &\quad - \frac{1}{Z} \frac{s}{4u t^2} + O\left(\frac{1}{Z^2}\right). \end{aligned} \quad (64)$$

Truncating 64 according to the prescription at the end of section 6 to obtain \tilde{m}_{1E} we note that for \tilde{m}_{1E} to match r_{1E} we must choose

$$a_0 = \frac{1}{2} \log Z. \quad (65)$$

Now that we have determined M_1 completely, to obtain the expansion near $\xi = 0$ we partially integrate 59b to increasing powers of V obtaining

$$g(V) = e^V \left[-\frac{2}{V^{1/2}} + 4V^{1/2} \left(1 - \frac{2}{3} V - \frac{2^2}{3 \cdot 5} V^2 + \dots \right) \right] \quad (66)$$

which leads to

$$\phi(V) \approx \frac{1}{2} \log(V-V) + \sum_{j=2} \frac{\varepsilon^{j-1} V^j}{[1 \cdot 3 \cdots (2j-1)](j)}. \quad (67)$$

In terms of our variables ξ and s

$$\begin{aligned} \phi &\approx \frac{1}{2} \log \frac{\xi^2}{2s} - \frac{1}{2} \frac{\xi^2}{s} + O\left(\frac{\xi^4}{s}\right) \\ \phi &\approx \log \xi - \frac{1}{2} \log 2s - \frac{1}{2} \frac{\xi^2}{s} \end{aligned} \quad (68)$$

Substituting into (55) for ξ^2/s small we obtain

$$M_1 \approx -\frac{1}{2} \log 2s + \frac{1}{2} \log Z - \frac{1}{2} \frac{\xi^2}{s} \quad (69)$$

and our solution m_1 no longer shows the singularity for t small which appeared in the original asymptotic expansion r_1 . Thus the correct solution to be used in region Ia is

$$\begin{aligned} m_1 = & \lambda \log \frac{s^2}{4} + \frac{1}{2}[\lambda^2 - c_2^2]s \\ & + \frac{s}{2u} \left[-\frac{1}{2} \log Z - \log 2u + \log(1 + \frac{u}{s}) + \frac{1}{2} \log 2s \right. \\ & \left. + \frac{1}{2} \frac{Zt^2}{s} + O\left(\frac{Zt^2}{s}\right)^2 \right]. \end{aligned} \quad (70)$$

Now let us consider region Ib. We choose the stretching

$$\xi = Z^{1/2}t$$

$$\gamma = Zu.$$

Therefore

$$\psi_1 = e^{-(Z-\lambda)s} \left[1 + \frac{1}{Z} \left[\lambda \log \frac{s^2}{4} \left(1 - \frac{\xi^2}{Zs^2} \right) + \frac{1}{2} [\lambda^2 - c_2^2]s + \tilde{c}_{12} \right] \right]$$

with

$$c_{12} = -\frac{1}{2d_1} \log \left(\frac{\gamma/Z + d_1 s}{(1+d_1) |\xi/Z^{1/2}|} \right) \quad (71)$$

and

$$d_1 = \sqrt{\frac{\frac{\gamma^2}{Z^2} - \frac{\xi^2}{Z}}{\frac{s^2}{Z^2} - \frac{\xi^2}{Z}}} \quad (71a)$$

For large Z

$$d_1 \approx \frac{i\xi}{Z^{1/2}s} \left[1 + \frac{1}{2Z} \left[\frac{\xi^2}{s^2} - \frac{\gamma^2}{\xi^2} \right] \right]$$

leading to

$$c_{12} \sim -\frac{Z^{1/2}}{4} \frac{1}{|\xi|} \left[\frac{s}{|\xi|} + \frac{1}{2} \left[\frac{su}{\xi^2} + 1 \right] \right] \quad (72)$$

Truncating (keeping 3 terms this time) we find

$$\begin{aligned} \psi_{1E} = e^{-(Z-\lambda)s} & \left(1 - \frac{1}{Z^{1/2}} \prod_{k=1}^{\infty} \frac{s}{1+k\xi} + \frac{1}{Z} \left(\lambda \log \frac{s^2}{4} + \frac{1}{2} [\lambda^2 - c_2^2] s \right. \right. \\ & \left. \left. + \frac{1}{2} \left[\frac{s\gamma}{\xi^2} + 1 \right] \right) + O\left(\frac{1}{Z^{3/2}}\right) \right). \end{aligned} \quad (73)$$

Now from the appendix we see that the equation for m_1 in region Ib takes the form

$$\frac{\partial^2 m_1}{\partial \gamma^2} + 2 \frac{\xi}{\gamma} \frac{\partial^2 m_1}{\partial \gamma \partial \xi} + 2 \left(\frac{\xi^2}{\gamma s} + \frac{1}{\gamma} \right) \frac{\partial m_1}{\partial \gamma} - \frac{1}{\gamma} = 0. \quad (74)$$

Using a power series construct as in case Ia we are led to an m_1 of the form

$$m_1 = a_0(s) + \gamma \chi(w) \quad (75)$$

where $w = \xi^2/s$ as before. Substituting (75) into (74) we find that $\chi(w)$ satisfies

$$4w \frac{d\chi}{dw} + 2[w+1]\chi - 1 = 0 \quad (76)$$

which has the solution

$$\chi = C \frac{1}{w^{1/2}} e^{-w/2} + \frac{1}{4w^{1/2}} e^{-w/2} \int_{-\infty}^w \frac{1}{w^{1/2}} e^{w/2} dw. \quad (77)$$

In order that our solution be even in t we choose $C = 0$.

For w large we integrate by parts to obtain

$$\chi(w) \sim \frac{1}{2w} \left(1 + \frac{1}{w} + O\left(\frac{1}{w^2}\right) \right). \quad (78)$$

For Z large, w large, comparison with (73) indicates that

one should take

$$a_0 = \lambda \log s^2/4 + 1/2[\lambda^2 - c_2^2]s + 1/2 \quad (79)$$

in order to match everything except the $1/z^{1/2}$ term.

Now for t small, w small one can integrate (77) to higher powers of w to obtain

$$\chi(w) = 1/2 \sum_{n=0}^{\infty} (-1)^n \frac{1}{3 \cdot 5 \cdots (2n+1)} w^n. \quad (80)$$

We now note that if we had included an $m_{1/2}/z^{1/2}$ term in expansion 42, $m_{1/2}$ would have satisfied the homogeneous part of equ. (74) and any function $m_{1/2}(s, \xi)$ is an acceptable solution. We shall now show that $m_{1/2}$ can not enter our asymptotic solution in the neighborhood of $\xi \approx 0$.

Let us first write down our asymptotic solution in region Ib as

$$\begin{aligned} \bar{\psi} &\approx e^{-(Z-\lambda)s} [1 + (1/2)u(1 - \frac{1}{3}(\frac{Zt^2}{s}) + o(\frac{Zt^2}{s})^2) \\ &+ \frac{m_{1/2}(s, \xi)}{z^{1/2}} + \frac{1}{Z}(\lambda \log s^2/4 + 1/2(\lambda^2 - c_2^2)s + 1/2)]. \end{aligned} \quad (81)$$

From part B of section 6 we expect that in region Ib

$$\frac{\partial \psi}{\partial u}(\xi, \gamma, s) \approx o(z^{1/2}) \frac{\partial \psi}{\partial t}(\xi, \gamma, s). \quad (82)$$

One observes that

$$\begin{aligned}
\frac{\partial \psi}{\partial t} &\approx e^{-(Z-\lambda)s} \left[-\frac{1}{12s} Z tu + \frac{1}{Z^{1/2}} \frac{\partial m_1}{\partial t} \right] = \\
&= e^{-(Z-\lambda)s} \left[-\frac{\xi \gamma}{12s} \frac{1}{Z^{1/2}} + \frac{1}{Z^{1/2}} \frac{\partial m_1}{\partial t} \right]
\end{aligned} \tag{83a}$$

and

$$\frac{\partial \psi}{\partial u} \approx e^{-(Z-\lambda)s} \frac{1}{2}. \tag{83b}$$

Now assume $m_1(s, \xi)$ is expressible as a power series about $\xi = 0$. For any power j

$$\frac{\partial m_1^j}{\partial t} \sim Z^{j/2} t^{j-1} = j \xi^{j-1} Z^{1/2}. \tag{84}$$

This would contribute a term of order Z^0 in $\frac{\partial \psi}{\partial t}$ in addition to the term already present of order $Z^{-1/2}$ and condition (82) would not then be fulfilled. Thus in the vicinity of $\xi \approx 0$, m_1 must vanish identically and therefore will not contribute to (81). Thus finally for the solution in region Ib we write

$$\begin{aligned}
\psi &\approx e^{-(Z-\lambda)s} \left[1 + 1/2 u \left(1 - \frac{1}{2} \left(\frac{Zt^2}{s} \right) + O \left(\frac{Zt^2}{s} \right)^2 \right) \right. \\
&\quad \left. + \frac{1}{Z} (\lambda \log s^2 / 4 + 1/2 (\lambda^2 - c_2^2) s + 1/2) \right]
\end{aligned} \tag{81a}$$

Now according to a theorem proved by Kato⁽¹⁶⁾, the exact wave function satisfies the cusp condition at $u = 0$ of the form

$$\left. \frac{\frac{\partial \psi}{\partial u}}{\psi} \right|_{u=0, t=0} = 1/2 \tag{82}$$

Performing these operations on our solution 81a we find that

$$\left. \frac{\partial \psi}{\partial u} \right|_{\begin{array}{l} \psi \\ u=0 \\ t=0 \end{array}} = [1 - \frac{1}{Z}(\lambda \log s^2/4 + s + 1/2)]. \quad (83)$$

Therefore in the limit that $Z \rightarrow \infty$ this cusp condition is identically satisfied.

In order to obtain our expansion for one or both of the electrons near the origin, it is convenient to rewrite the Schrodinger 2 electron Equation in terms of variables s_1, s_2, u .

$$\begin{aligned} & \frac{\partial^2 \psi}{\partial s_1^2} + \frac{2}{s_1} \frac{\partial \psi}{\partial s_1} + \frac{\partial^2 \psi}{\partial s_2^2} + \frac{2}{s_2} \frac{\partial \psi}{\partial s_2} + 2 \frac{\partial^2 \psi}{\partial u^2} \\ & + \frac{4}{u} \frac{\partial \psi}{\partial u} \frac{(s_1^2 - s_2^2 + u^2)}{s_1 u} \frac{\partial^2 \psi}{\partial s_1 \partial u} + \frac{(s_2^2 - s_1^2 + u^2)}{s_2 u} \frac{\partial^2 \psi}{\partial s_2 \partial u} \\ & + 2(E + \frac{Z}{s_1} + \frac{Z}{s_2} - \frac{1}{u})\psi = 0 . \end{aligned} \quad (84)$$

For the case that electron 1 is near the nucleus, let us assume an integral stretching of the form $\xi_1 = Zs_1$ is correct. Noting that in terms of u, s_1 , and s_2 , d in r_1 is expressed as

$$d = \left[\frac{u^2 - (s_2 - s_1)}{4s_1 s_2} \right]^{1/2}, \quad (85)$$

we can write

$$\begin{aligned}\psi_1 = & e^{-(Z-\lambda)s_2} e^{-\xi_1} e^{-\lambda \xi_1/Z} \left(1 + \frac{1}{Z} [\lambda(\ln \frac{\xi_1}{Z} + \ln s_2) \right. \\ & \left. + \frac{1}{2} (\lambda^2 - c_2^2) (\frac{\xi_1}{Z} + s_2) + \zeta_{12}] \right)\end{aligned}\quad (86)$$

with

$$\zeta_{12} = -\frac{1}{2\xi_1} \log \left(\frac{u + \frac{\xi_1}{Z} + s_2}{(1 + \frac{\xi_1}{Z})(s_2 - \frac{\xi_1}{Z})} \right)$$

and

$$\xi_1 = \left[\frac{u^2 - (s_2 - \frac{\xi_1}{Z})^2}{4 \frac{\xi_1}{Z} s_2} \right]^{1/2} . \quad (86a)$$

For large Z

$$\xi_1 \approx \frac{Z^{1/2}}{2} \left[\frac{u^2 - s_2^2}{\xi_1 s_2} \right]^{1/2} . \quad (86b)$$

which leads to an expansion for Z large of the form

$$\zeta_{12} \approx -\frac{\xi_1}{Z} \left[\frac{\xi_1}{u + s_2} \right] + O(\frac{1}{Z^2}) . \quad (87)$$

Therefore truncating to two orders

$$\begin{aligned}\xi_{1E} = & e^{-(Z-\lambda)s_2} e^{-\xi_1} e^{-\lambda \xi_1/Z} + \frac{1}{Z} (-\lambda \ln Z + \lambda \xi_1 \\ & + \lambda \ln \xi_1 + \lambda \ln s_2 + 1/2 (\lambda^2 - c_2^2) s_2) .\end{aligned}\quad (88)$$

This suggests that we look for a solution of the stretched equation of the form

$$\bar{\psi} = e^{-(Z-\lambda)s_2} e^{-\xi_1} \left(1 + \frac{1}{Z} [m_1^{(1)}(\xi_1) + m_1^{(2)}(s_2)] + \frac{1}{Z^2} m_2 + \dots \right). \quad (89)$$

Making this ansatz and substituting into the stretched P.D.E.

$$\begin{aligned} & Z^2 \left[\frac{\partial^2 \psi}{\partial \xi_1^2} + \frac{2}{\xi_1} \frac{\partial \psi}{\partial \xi_1} \right] + \frac{\partial^2 \psi}{\partial s_2^2} + \frac{2}{s_2} \frac{\partial \psi}{\partial s_2} + 2 \frac{\partial^2 \psi}{\partial u^2} + \frac{4}{u} \frac{\partial \psi}{\partial u} \\ & + \frac{\xi_1}{u} \frac{\partial^2 \psi}{\partial \xi_1 \partial u} - Z^2 \frac{s_2^2}{\xi_1^2 u} \frac{\partial^2 \psi}{\partial \xi_1 \partial u} + Z^2 \frac{u}{\xi_1} \frac{\partial^2 \psi}{\partial \xi_1 \partial u} \\ & + \left[\frac{s_2}{u} - \frac{1}{Z^2} \frac{\xi_1^2}{us_2} + \frac{u}{s_2} \right] \frac{\partial^2 \psi}{\partial s_2 \partial u} \\ & + 2(-Z^2(c_0^2 - Z^{-1}c_1^2 + Z^{-2}c_2^2 + \dots) + \frac{Z^2}{\xi_1} + \frac{Z}{s_1} - \frac{1}{u})\psi = 0 \end{aligned} \quad (90)$$

we obtain from setting the coefficient of $Z^{(1)}$ terms equal to 0

$$\frac{\partial^2 m_1^{(1)}}{\partial \xi_1^2} + \left[\frac{2}{\xi_1} - 2 \right] \frac{\partial m_1^{(1)}}{\partial \xi_1} = -c_1^2. \quad (91)$$

A solution of this equation is

$$m_1^{(1)} = \lambda [\xi_1 + \ln \xi_1 - \frac{1}{2\xi_1} - \frac{1}{2} \int_{-\infty}^{\xi_1} \frac{d\xi_1 e^{2\xi_1}}{\xi_1^2} + C] \quad (92)$$

where C is a constant to be determined.

From setting the coefficient of the $Z^{(0)}$ terms equal to 0 we obtain

$$\begin{aligned}
& -2\left[\frac{\partial m_1^{(2)}}{\partial s_2} - \frac{\lambda}{s_2} + \frac{1}{2}[c_2^2 - \lambda^2]\right] \\
& + \frac{\partial^2 m_2}{\partial \xi_1^2} + 2\left[\frac{1}{\xi_1} - 1\right] \frac{\partial m_2}{\partial \xi_1} \\
& - c_2^2 + c_1^2[m_1^{(1)} + m_1^{(2)}] \\
& + \frac{1}{\xi_1 u} [u^2 - s_2^2] \left[\frac{\partial m_2}{\partial u} + \frac{\partial^2 m_2}{\partial u \partial \xi_1} \right] - \frac{2}{u} = 0.
\end{aligned} \tag{93}$$

Choosing to set the first parenthesis itself equal to 0 we obtain

$$m_1^{(2)} = \lambda \ln s_2 + 1/2[\lambda^2 - c_2^2]s_2. \tag{94}$$

For Z large we can rewrite

$$m_1^{(1)} \approx \lambda[Zs_1 + \ln Zs_1 - \frac{1}{2Zs_1} - \frac{1}{2Z}] \int_{-\infty}^{Zs_1} ds_1 \frac{e^{-\frac{s_1}{Z}}}{s_1} + C \tag{92a}$$

and performing the usual truncation procedure

$$m_1^{(1)} \approx \lambda[Zs_1 + \ln Zs_1 + O(\frac{1}{Z}) + C]. \tag{92b}$$

Considering (94) and (92b) in 89 we observe that the matching condition with (88) is made if we choose

$$C = -\ln Z. \tag{95}$$

Thus the matched stretched solution is

$$\begin{aligned}\bar{\psi} = & e^{-(Z-\lambda)s_2} e^{-\xi_1} [1 + \frac{1}{Z} [\lambda \ln s_2 + \frac{1}{2} / 2(\lambda^2 - c_2^2) s_2 \\ & + \lambda(\xi_1 + \ln \xi_1 - \frac{1}{2\xi_1}) - \frac{1}{2} \int_{-\infty}^{\xi_1} \frac{d\xi e^{2\xi}}{\xi^2} - \ln Z)]]. \quad (96)\end{aligned}$$

To obtain the expansion for s_1 small, we integrate by parts to higher powers of ξ to obtain

$$\begin{aligned}\bar{\psi} = & e^{-(Z-\lambda)s_2} e^{-\xi_1} [1 + \frac{1}{Z} [-\lambda \ln Z + \lambda \ln s_2 + \frac{1}{2} / 2(\lambda^2 - c_2^2) s_2 \\ & - \lambda(\frac{\xi_1^2}{3} + O(\xi_1^3))]]\end{aligned}$$

and therefore

$$\begin{aligned}\bar{\psi} = & e^{-(Z-\lambda)s_2} e^{-Zs_1} [1 - \frac{\lambda}{Z} (\frac{(Zs_1)^2}{3} + O(Zs_1)^3) \\ & + \frac{1}{Z} [-\lambda \ln Z + \lambda \ln s_2 + \frac{1}{2} / 2(\lambda^2 - c_2^2) s_2]] \quad (97)\end{aligned}$$

for the case of s_1 small (in region IIa). Thus the correct asymptotic expansion has no divergences at $s_1 = 0$. The solution shows the expected physical characteristic that for one electron very near to the origin the shielding effect of the outer electron upon it goes to 0.

The cusp condition at $s_1 = 0$ satisfied exactly by the correct wave function is

$$\left. \frac{\frac{\partial \psi}{\partial s_1}}{\psi} \right|_{s_1=0} = -Z. \quad (98)$$

Now for our asymptotic solution (97)

$$\frac{\partial \bar{\psi}}{\partial s_1} = -Z\bar{\psi} + e^{-(Z-\lambda)s_2} e^{-zs_1} \left[\frac{-2Z\lambda s_1}{3} + O(s_1^2) \right] \quad (99)$$

which in the limit $s_1 = 0$ becomes

$$\left. \frac{\partial \bar{\psi}}{\partial s_1} \right|_{s_1=0} = -Z\bar{\psi}(s_1=0). \quad (100)$$

Our asymptotic solution identically satisfies this cusp condition.

In section Ia we perform additional integral stretching on s_2 and u . We define $\xi_1 = Zs_1$, $\xi_2 = Zs_2$ and $\gamma = Zu$. One can readily show that for this case

$$\begin{aligned} \underline{\psi}_{1E} = & e^{-(\xi_2+\xi_1)} \left[1 + \frac{1}{Z} [-2\lambda \ln Z + \lambda(\xi_1 + \xi_2) \right. \\ & \left. + \lambda(\ln \xi_1 + \ln \xi_2) + c_{12}(\xi_1, \xi_2, \gamma)] \right] \end{aligned} \quad (101)$$

with

$$c_{12}(\xi_1, \xi_2, \gamma) = -\frac{1}{2d} \ln \left(\frac{\gamma + d(\xi_1 + \xi_2)}{(1+d)|\xi_2 - \xi_1|} \right)$$

and

$$d = \left(\frac{\gamma^2 - (\xi_2 - \xi_1)^2}{4\xi_1 \xi_2} \right)^{1/2}.$$

Transforming equation 84 to new coordinates we obtain the usual "perturbation theory" equation in the form

$$\begin{aligned}
& \frac{\partial^2 \psi}{\partial \xi_1^2} + \frac{2}{\xi_1} \frac{\partial \psi}{\partial \xi_1} + \frac{\partial^2 \psi}{\partial \xi_2^2} + \frac{2}{\xi_2} \frac{\partial \psi}{\partial \xi_2} + 2 \frac{\partial^2 \psi}{\partial \gamma^2} \\
& + \frac{4}{\gamma} \frac{\partial \psi}{\partial \gamma} + \frac{(\xi_1^2 - \xi_2^2 + u^2)}{\xi_1 u} \frac{\partial^2 \psi}{\partial \xi_1^2 u} + \frac{(\xi_2^2 - \xi_1^2 + u^2)}{\xi_2 u} \frac{\partial^2 \psi}{\partial \xi_2^2 u} \\
& + 2((-c_0^2 + z^{-1} c_1^2 - z^{-2} c_2^2 + \dots) + \frac{1}{\xi_1} + \frac{1}{\xi_2}) \psi - \frac{1}{z} \frac{2}{\gamma} \psi = 0.
\end{aligned} \tag{102}$$

We look for a solution of 102 of the form

$$\begin{aligned}
\bar{\psi} = e^{-(\xi_1 + \xi_2)} & \left(1 + \frac{1}{z} [m_1^{(1)}(\xi_1) + m_1^{(2)}(\xi_2) + M_1(\xi_1, \xi_2, u)] \right. \\
& \left. + \frac{1}{z^2} m_2(\xi_1, \xi_2, u) + \dots \right). \tag{103}
\end{aligned}$$

Substituting (103) into (102) one finds that $m_1^{(1)}$ and $m_1^{(2)}$ satisfy equations of the form (91) in their respective variables. Therefore from the analysis for section IIa it follows that $m_1^{(1)}$ and $m_1^{(2)}$ will be matched with the first three terms of the coefficient of $1/z$ in equation (101).

We find the remaining equation satisfied by M_1 to be

$$\begin{aligned}
& \frac{\partial^2 M_1}{\partial \xi_1^2} + 2[\frac{1}{\xi_1} - 1] \frac{\partial M_1}{\partial \xi_1} + \frac{\partial^2 M_1}{\partial \xi_2^2} + 2[\frac{1}{\xi_2} - 1] \frac{\partial M_1}{\partial \xi_2} \\
& + 2 \frac{\partial^2 M_1}{\partial \gamma^2} + \frac{4}{\gamma} \frac{\partial M_1}{\partial \gamma} - [\frac{\xi_1^2 - \xi_2^2 + \gamma^2}{\xi_1 \gamma} + \frac{\xi_2^2 - \xi_1^2 + \gamma^2}{\xi_2 \gamma}] \frac{\partial M_1}{\partial \gamma}
\end{aligned}$$

$$+ \left[\frac{\xi_1^2 - \xi_2^2 + \gamma^2}{\xi_1 \gamma} \right] \frac{\partial^2 M_1}{\partial \xi_1 \partial \gamma} + \left[\frac{\xi_2^2 - \xi_1^2 + \gamma^2}{\xi_2 \gamma} \right] \frac{\partial^2 M_1}{\partial \xi_2 \partial \gamma} = - \frac{2}{\gamma} . \quad (104)$$

Since we have already taken proper care of the functions depending only on either variable ξ_1 or ξ_2 near the origin with our choice of $m_1^{(1)}$ and $m_1^{(2)}$ we expect that near the origin

$$M_1 = C\gamma + O(\gamma\ell) \quad (105)$$

where C is a constant to be determined and ℓ represents one of the fundamental smallness distances γ , ξ_1 or ξ_2 . Substitution of (105) into (104) gives $C = 1/2$. Although we have not shown the matching condition fulfilled for M_1 with C_{12} we have determined the leading term of M_1 near the origin. Thus for region IIb keeping only the leading terms of $m_1^{(1)}$ and $m_1^{(2)}$ we have

$$\bar{\psi} \approx e^{-Zs_1} e^{-Zs_2} \left[1 - 2\lambda \frac{\ln Z}{Z} + (1/2)u - \frac{\lambda Z}{3} (s_1^2 + s_2^2) + O\left(\frac{\gamma\ell}{Z}\right) \right]. \quad (106)$$

assuming no other constants are brought in by matching M_1 . Note that 106 identically satisfies the cusp condition (98) for s_1 or s_2 equal to 0. The cusp condition at $u = 0$ is exactly satisfied in the limit that $Z \rightarrow \infty$. Thus in the neighborhood of the origin

$$\psi \approx 1 - Z(s_1 + s_2) + 1/2u - 2\lambda \frac{\ln Z}{Z} + O(\ell^2) \quad (106a)$$

in the limit of infinite Z our ψ gives correct⁽¹⁷⁾ behavior. This is to be compared with perturbation theory where the coefficient of the u term near the origin does not go over to its exact theoretical value in the infinite Z case⁽¹⁸⁾. Since ordinary perturbation theory assumes at the outset no $\log Z$ terms are present in the wave function expansion whereas we have shown that in certain spacial regions they must be included, it is not surprising that the perturbation theory wave functions and expectation values calculated from them will show certain failings.

APPENDIX I. Ordering of Terms for a Coordinate Stretching

ASY EXP A	-	j=0,	k=0
ASY EXP Ta	-	j=0,	$\frac{1}{2}$
ASY EXP Tb	-	j=1,	$\frac{1}{2}$

$$us^2 \left[\frac{z^2}{z} + Z(m_1 - 2\lambda) + \lambda \begin{bmatrix} -2\lambda m_1 \\ m_2 \end{bmatrix} \right] \begin{array}{l} \text{Ia} \\ \text{A} \\ (-j) \end{array} \quad \begin{bmatrix} \text{Ia} \\ \text{A} \\ (-j) \end{bmatrix} \begin{bmatrix} \frac{\partial m_1}{\partial s} - 2 \\ \frac{\partial m_1}{\partial s} + \frac{1}{2}(2\lambda m_2 - 2) \end{bmatrix} \begin{bmatrix} \frac{\partial m_1}{\partial t} + 2\lambda \\ \frac{\partial s}{\partial t} \end{bmatrix} \begin{bmatrix} \text{Ia} \\ \text{B} \\ (-j-1) \end{bmatrix} \quad \begin{bmatrix} \text{Ia} \\ \text{B} \\ (-j-1) \end{bmatrix} \begin{bmatrix} \frac{\partial^2 m_1}{\partial u^2} + \frac{\partial^2 m_1}{\partial t^2} \\ \frac{\partial^2 m_1}{\partial u^2} \end{bmatrix} \begin{bmatrix} \text{Ib} \\ (-j-1) \end{bmatrix}$$

$$A = \begin{bmatrix} -ut^2 & Z(m_1 - Z\lambda) + \lambda^2 \\ Z^2 + Z(m_1 - Z\lambda) & m_2 - 2\frac{\partial m_1}{\partial s} + \frac{1}{Z}(2\lambda m_2 - 2\frac{\partial m_1}{\partial s} + \frac{\partial^2 m_1}{\partial s^2} + \frac{\partial^2 m_1}{\partial t^2} + \frac{\partial^2 m_1}{\partial u^2}) \end{bmatrix}$$

$$+2su^2 \left[-\frac{\partial m_1}{\partial u} + \frac{1}{Z} \left(\frac{\partial^2 m_1}{\partial s \partial u} - \frac{\partial m_2}{\partial u} + \lambda \frac{\partial m_1}{\partial u} \right) \right]$$

$$\text{Ib} \quad -2st^2 \left[-\frac{\partial m_1}{\partial u} + \frac{1}{Z} \left(\frac{\partial^2 m_1}{\partial s \partial u} - \frac{\partial m_2}{\partial u} + \lambda \frac{\partial m_1}{\partial u} \right) \right] \\ \left(\begin{array}{l} j-2k \\ j-2k-1 \end{array} \right) \left(\begin{array}{l} j-2k-1 \\ j-2k-1 \end{array} \right)$$

$$\begin{aligned}
& + 2ts^2 \left[\frac{1}{Z} \frac{\partial^2 m_1}{\partial u \partial t} \right] - 2t u^2 \left[\frac{1}{Z} \frac{\partial^2 m_1}{\partial u \partial t} \right] \\
& (-j-1) \quad \quad \quad (-j-1)
\end{aligned}$$

$$\begin{aligned}
& I_a \\
& + 4su(-Z) + \lambda \boxed{-m_1} + \frac{1}{Z} \left(\frac{\partial m_1}{\partial s} - m_2 + \lambda m_1 \right) \\
& (-j) \quad \quad \quad (-j-1)(-j-1)(-j-1)
\end{aligned}$$

$$\begin{aligned}
& I_b \\
& + 2[s^2 - t^2] \frac{1}{Z} \frac{\partial m_1}{\partial u} - 4ut \frac{1}{Z} \frac{\partial m_1}{\partial t} \\
& (-j-1)(j-2k-1) \quad \quad \quad (-j-1)
\end{aligned}$$

$$\begin{aligned}
& I_a \\
& + 4zs u \left(\boxed{1} + \boxed{\frac{m_1}{Z}} \right) - s^2 \left(\frac{A}{Z} + \frac{m_1}{Z} \right) + t^2 \left(\frac{A}{Z} + \frac{m_1}{Z} \right) \\
& O(-1) \quad \quad \quad (-2k)(-2k-1) \\
& I_a \\
& + 4zs u \left(\boxed{1} + \boxed{\frac{m_1}{Z}} \right) - s^2 \left(\frac{A}{Z} + \frac{m_1}{Z} \right) + t^2 \left(\frac{A}{Z} + \frac{m_1}{Z} \right) \\
& + us^2(-Z^2) + z \left(\boxed{-m_1} + \boxed{C_1^2} \right) + \boxed{C_1^2 m_1} + \boxed{C_1^2} - C_2^2 \\
& (-j) \quad \quad \quad (-j) \\
& I_a \\
& + 4zs u \left(\boxed{1} + \boxed{\frac{m_1}{Z}} \right) - s^2 \left(\frac{A}{Z} + \frac{m_2}{Z} \right) + t^2 \left(\frac{A}{Z} + \frac{m_2}{Z} \right) - j-2k \\
& = 0.
\end{aligned}$$

Figure 1

$|S|^2$ CORRELATION FUNCTION OF $\theta_{12} = 0^\circ$

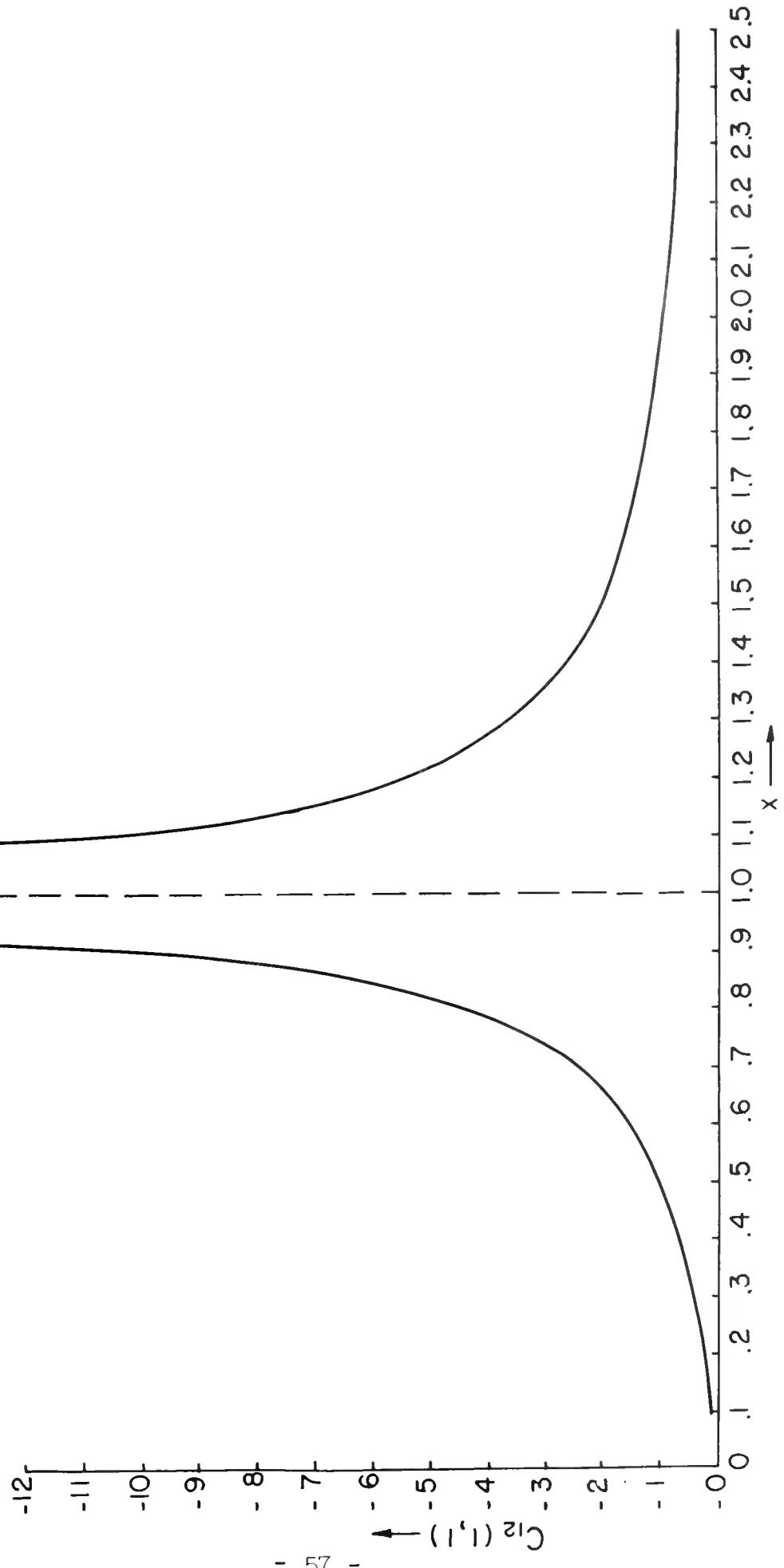
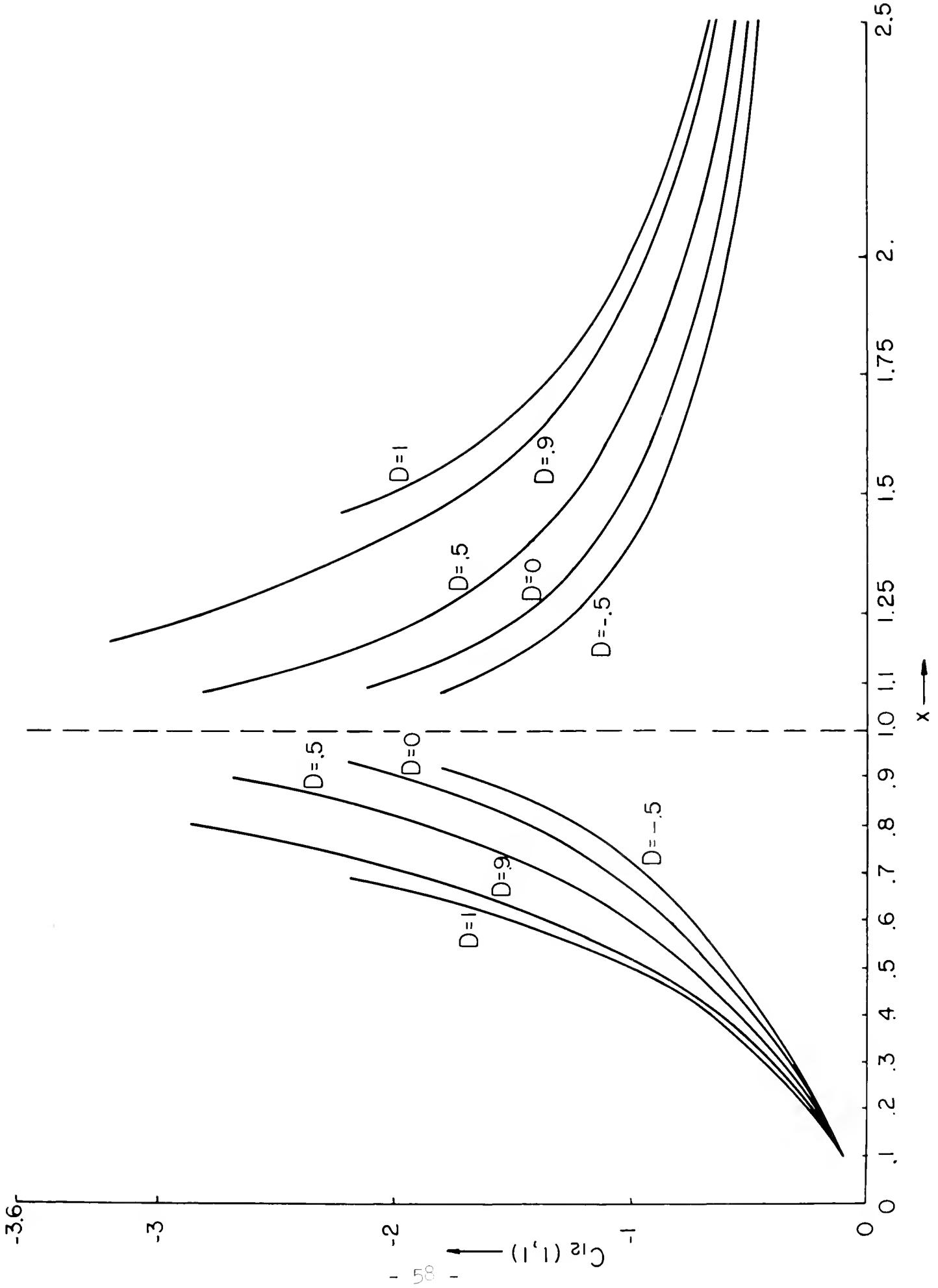


Figure 2



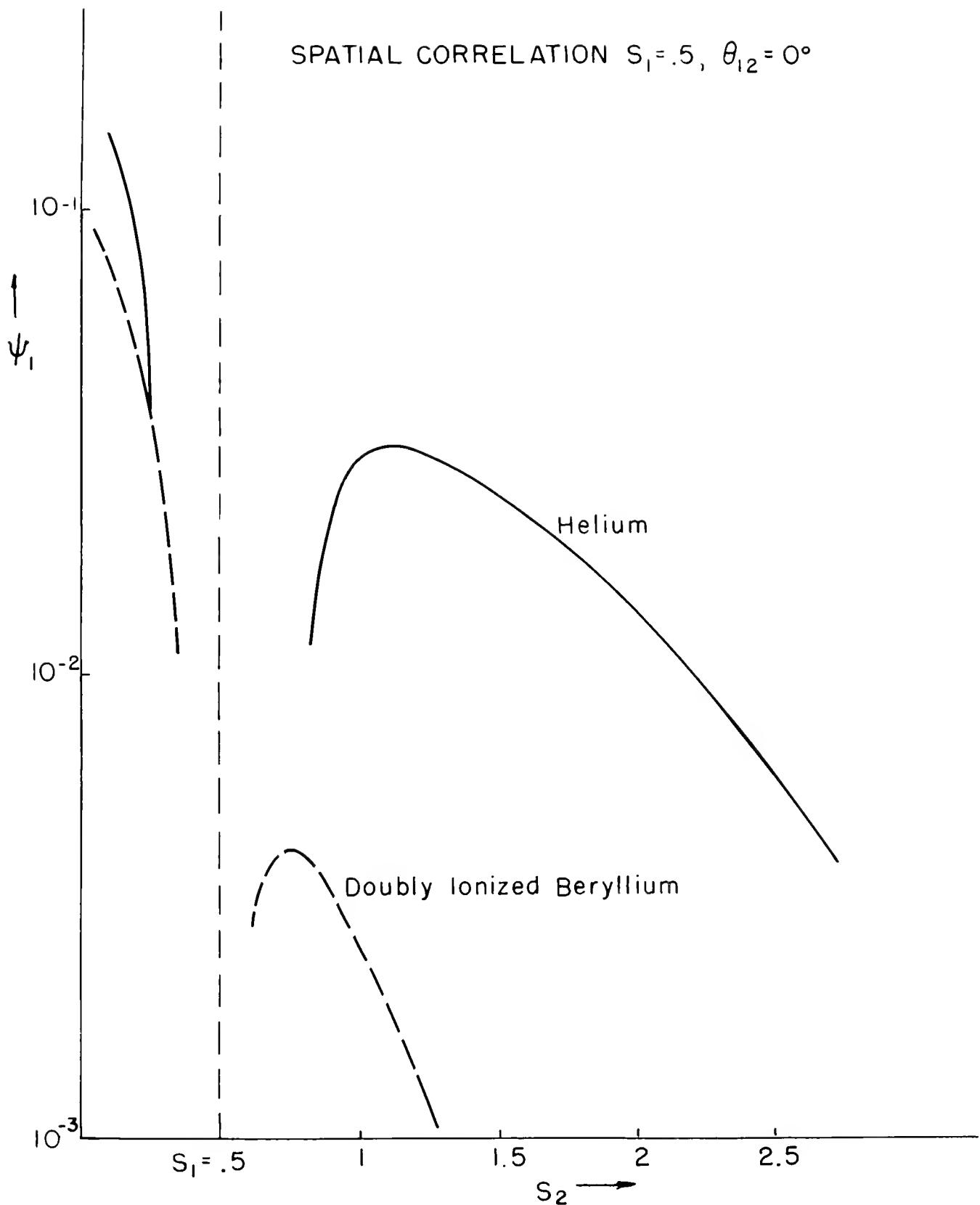


Figure 3 - 59 -

SPATIAL CORRELATION HELIUM
 $S_1 = 2.0, \theta_{12} = 0^\circ$

— $\psi_0 = e^{-1.6875(s_1 + s_2)}$
 - - - $\psi_1 = \psi_0(1 + Z^{-1}r_1)$

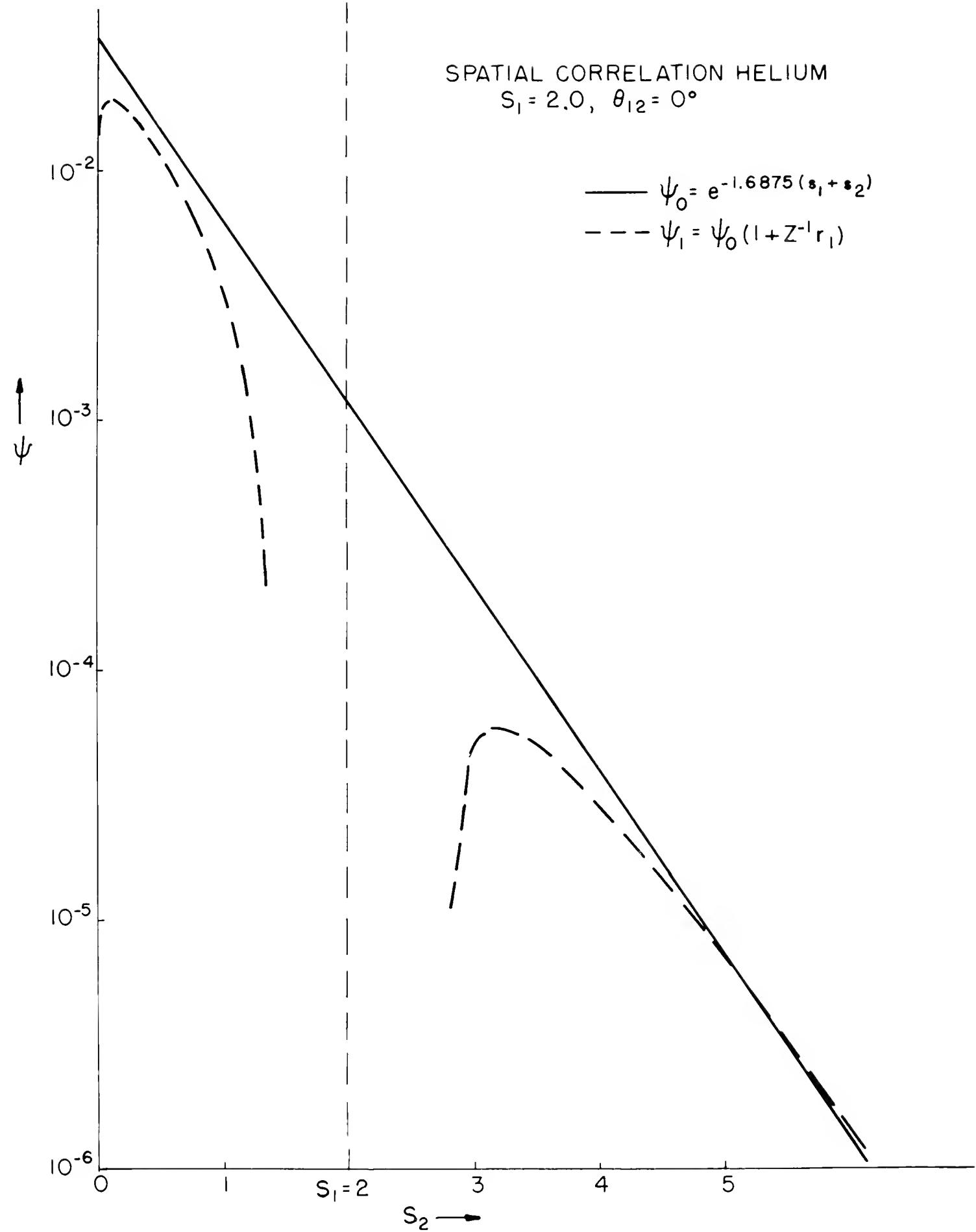


Figure 4

ANGULAR CORRELATION-HELIUM

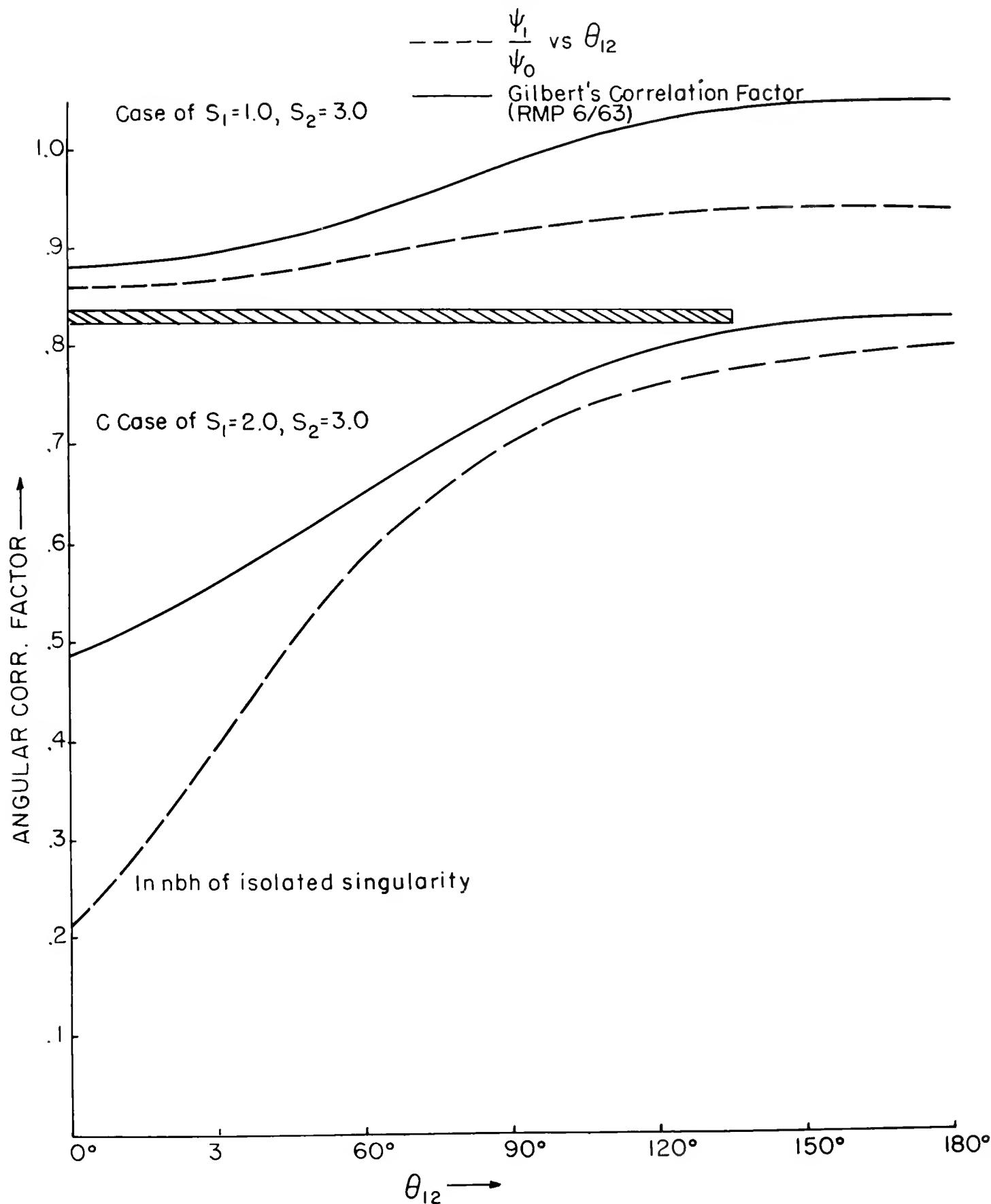


Figure 5

BIBLIOGRAPHY

- [1] Per-Olov Lowdin, Recent Development of the Theory of the Electronic Structure of Atoms, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (1958).
- [2] M. Cohen and A. Dalgarno, Rev. Mod. Phys. 35, 506(1963).
- [3] T. Kinoshita, Phys. Rev. 105, 1490(1957).
- [4] C. L. Pekeris, Phys. Rev. 112, 1649(1958).
C. L. Pekeris, Phys. Rev. 115, 1216(1959).
C. L. Pekeris, Phys. Rev. 126, 143(1962).
- [5] C. W. Scherr, J. M. Silverman and F. A. Matsen, Phys. Rev. 127, 830(1962).
- [6] R. M. Lewis and J. B. Keller, N.Y.U., EM Div., Research Report EM-194, (1964).
- [7a] Dalgarno and Stewart, Proc. Roy. Soc. 247, 245(1958).
- [7b] A. L. Stewart, Advances in Physics 47, 299(1963).
- [7c] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. 35, 436(1963).
- [8] R. Courant and D. Hilbert, Methods of Mathematical Physics Vol. 2 (Interscience Publishers Inc., New York, (1962)).
- [9] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two Electron Atoms (Springer-Verlag, Berlin, (1957)), pp. 153. Also see reference 5.

- [10] C. Schwartz, Phys. Rev. 126, 1015(1962).
- [11] T. L. Gilbert, Rev. Mod. Phys. 35, 431(1963).
- [12] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. 35, 431(1963).
- [13] Reference 9, pp. 147.
- [14] H. T. Davis, Tables of Higher Mathematical Functions (Principia Press, Indiana, (1933)).
- [15] Van Dyke, Perturbation Methods in Fluid Mechanics (Academic Press, New York, (1964)), pp. 90.
- [16] T. Kato, N.Y.U. Res. Rep't. CX-25, (1956).
- [17] V. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. 18, 161-172(1954).
- [18] Reference 12, pp. 435.

Acknowledgement

One of us (L.M.) would like to express thanks to Professor Werner Brandt and the New York University Solid State Laboratories where the initial phases of this work were done.

